The origin and emergence of life under impact bombardment

Charles S. Cockell*

*Centre for Earth, Planetary, Space and Astronomical Research, Open University,
Milton Keynes MK7 6AA, UK*

Craters formed by asteroids and comets offer a number of possibilities as sites for prebiotic chemistry, and they invite a literal application of Darwin's 'warm little pond'. Some of these attributes, such as prolonged circulation of heated water, are found in deep-ocean hydrothermal vent systems, previously proposed as sites for prebiotic chemistry. However, impact craters host important characteristics in a single location, which include the formation of diverse metal sulphides, clays and zeolites as secondary hydrothermal minerals (which can act as templates or catalysts for prebiotic syntheses), fracturing of rock during impact (creating a large surface area for reactions), the delivery of iron in the case of the impact of iron-containing meteorites (which might itself act as a substrate for prebiotic reactions), diverse impact energies resulting in different rates of hydrothermal cooling and thus organic syntheses, and the indiscriminate nature of impacts into every available lithology—generating large numbers of 'experiments' in the origin of life. Following the evolution of life, craters provide cryptoendolithic and chasmoendolithic habitats, particularly in non-sedimentary lithologies, where limited pore space would otherwise restrict colonization. In impact melt sheets, shattered, mixed rocks ultimately provided diverse geochemical gradients, which in present-day craters support the growth of microbial communities.

Keywords: organics; colonization; thermophiles; asteroid; crater

1. INTRODUCTION

During the Hadean, the surface of the Earth was subjected to relatively heavy bombardment by asteroid and comet impacts, compared to the surface of the present-day Earth (Nisbet & Sleep 2001; Kring & Cohen 2002; Ryder 2003).

Assuming that the origin of life occurred on Earth, it happened in an environment that was periodically disturbed. The impact flux on the early Earth was not only higher, but the frequency of large high-energy impacts was also higher. Although the impact events cause environmental disturbance, the craters associated with them might have characteristics that make them the suitable geochemical environments for prebiotic chemistry, particularly with respect to their hydrothermal systems. The role of impacts in the origin of life has not been examined in any detail. However, hydrothermal vents on the ocean floor have received attention as sites for the origin of life (e.g. Wächtershäuser 1988; Holm 1992; Russell & Hall 1997), and these environments, *mutatis mutandis*, might provide a basis from which to investigate the potential of impact-induced hydrothermal systems as sites for prebiotic chemistry.

Following the emergence of life, impacts would have had a profound influence on its distribution and characteristics. Between the time of the formation of the Earth and *ca* 3.8 Gyr ago, life in the oceans may have been periodically extirpated, if it existed at this

time (Sleep *et al.* 1989). Impactors larger than 500 km in diameter have been suggested to have sufficient energy to boil the whole ocean (Sleep *et al.* 1989) or to have at least boiled the top few hundred metres (Ryder 2003). These events would have favoured life in the deep regions of the Earth's crust below the oceans. The periodic global heating caused by impacts has been suggested as an explanation for the hyperthermophilic root of the phylogenetic tree of life (Maher & Stevenson 1988; Sleep *et al.* 1989). The hyperthermophilic root neither proves that life originated in hot conditions nor that the first organism need have been a hypothermophile; the tree of life merely suggests that, at some point in early history, a bottleneck resulted in the survival of hyperthermophiles that led to the diversity of life on Earth today (if the root of the phylogenetic tree is a reliable indication of the nature of Archaean microbiology, and not merely an artefact of present-day 16S RNA sequences).

It has been suggested that impact events would have provided an escape mechanism for life from these early ocean-sterilizing impacts. Modelling data suggest that micro-organisms could have been ejected into the refugium of interplanetary space on rocks launched during impact, to return and reseed the Earth several thousand years later (Wells *et al.* 2003). Wells' data suggest that with an initial cell population of 10^3 – 10^5 cells kg^{-1} , at least one cell in this material would return after 3000–5000 years, following a sterilizing impact. Qualitatively similar conclusions have recently been obtained by Gladman *et al.* (2005), who show that 1% of the impact-ejected material might eventually return to Earth.

*c.s.cockell@open.ac.uk

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It is apparent, based on the study of extant microbial communities within impact-altered target lithologies, that craters would not only have disturbed the early biosphere, but would have provided a suitable, and in some cases improved, geomicrobiological environment for early life. Certain lithological changes induced by impact would have improved the conditions for lithophytic organisms (Cockell *et al.* 2002).

In this paper, I do not propose a chemical theorem for the origin of life, but rather I will examine the characteristics of impact-induced hydrothermal systems and their associated craters as plausible sites for the origin and emergence of life.

2. CRATERS AND THE ORIGIN OF LIFE

Theories on the pathways of prebiotic evolution and the formation of the first complex self-replicating macromolecules have to take into account several common requirements, including: (i) a source of energy to drive molecular and macromolecular synthesis, (ii) a mechanism for the localized concentration of reactants to favour the required chemical reactions, (iii) suitable catalysis and (iv) a suitable geochemical environment for these reactions and their products to be sustained for sufficiently long periods to lead to the origin of life. This last requirement is important, because although specific chemical reactions might be theoretically favoured, these reactions have to occur in a real environment, not in laboratories or on a computer. This requires the identification of geochemical environments at the macroscale that offer promise as sites for the origin of life at the micro- and nano-scale.

A diversity of geochemical environments has been proposed as suitable sites to meet such requirements. Hydrothermal systems have received attention as sites for organic synthesis and the origin of life (e.g. Wächtershäuser 1988; Ferris 1992; Holm 1992; Russell *et al.* 1998; Simoneit 2004). At plate boundaries and above magma plumes, hydrothermal fluids would have provided a source of heat and chemical energy, in the form of reactive minerals, to sustain prebiotic reactions.

A sufficient concentration of reactants is difficult to imagine in the open oceans, where dilution does not favour the required local conditions for prebiotic reactions. However, mineral surfaces, such as clays, can potentially provide templates, surfaces for sorption, and even catalysis of chemical reactions (Goldschmidt 1952; Rao *et al.* 1980; Cairns-Smith 1982; Ponnamperna *et al.* 1982; Ferris *et al.* 1988; Cairns-Smith *et al.* 1992; Lahav 1994).

In theories on the origin of life, asteroid and comet impacts generally have been regarded as inimical to these early prebiotic syntheses. The suggested migration of acetogenic precursors of life into the deep subsurface (Russell & Arndt 2005) meets the need to escape the hostile surface conditions associated with impact.

However, craters associated with impacts provide many required geochemical conditions that favour prebiotic reactions. Many of these conditions are contemporaneous during post-impact environmental

changes. Thus, craters provide a suite of conditions, which, taken together, make them plausible realistic environments for sustained experiments in the origin of life. I will examine each of these characteristics.

(a) *Source of energy and precursors*

Impactors themselves might have delivered organic precursors for the origin of life (Chyba & Sagan 1992; Maurette 1998; Charnley *et al.* 2002), since some of these precursors would have survived impact (Pierazzo & Chyba 1999). Organics might have been generated by shock processing of the atmosphere (Fegley *et al.* 1986) or during impact itself (McKay & Borucki 1997), some of which might have been washed into hydrothermal systems from previous impacts, to be incorporated into the breccias and suevites. However, impact hydrothermal systems could have provided conditions for the *de novo* synthesis of a diversity of organic compounds. Numerous previous studies have addressed the possibility of organic synthesis in deep-ocean hydrothermal systems (e.g. Corliss *et al.* 1981; Baross & Hoffman 1985; Shock 1990) and these studies illuminate the potential for organic synthesis in impact-induced hydrothermal systems. Shock & Schulte (1998), using theoretical modelling, show that dynamic fluid mixing (as would have occurred deep in impact craters or following impact events into the Hadean oceans, where hydrothermal fluids mixed with Hadean seawater) can yield organic compounds such as carboxylic acids, alcohols and ketones, which are thermodynamically stable in hydrothermal systems. The formation of organic compounds from CO₂ and H₂ within impact hydrothermal systems would have provided a continuous source of precursors for oligomerization reactions, in addition to exogenous organics; these latter sources eventually becoming depleted. The CO₂ for hydrothermal synthesis would have been derived from the Hadean atmosphere and the H₂ would have been derived from volcanic outgassing and/or the atmosphere (Tian *et al.* 2005), or the reaction of water with impact-fractured basalts within the crater and its fractured surroundings, through the process of serpentinization (Moody 1976; Neal & Stanger 1983; Berndt *et al.* 1996). The impact-induced fracturing of the basement rock could have caused a 'pulse' of serpentinization to fuel early organic formation during the onset of the hydrothermal system. Empirical evidence for the production of hydrocarbons and organics through serpentinization has been presented for the crystalline rocks of the Canadian and Fennoscandian Shields (Sherwood Lollar *et al.* 1993) and Conical Seamount in the Mariana forearc (Haggerty 1991; Haggerty & Fisher 1992). The production of hydrocarbons on fresh olivine surfaces cracked by volcanically induced expansion and contraction has been suggested (Tingle & Hochella 1993), indirectly supporting the notion of a role for impact-induced fracturing in providing surfaces for serpentinization and later hydrocarbon formation, although laboratory experiments simulating the volcanic process have been more equivocal (Tingle & Hochella 1993).

(b) Appropriate minerals for prebiotic reactions

Impact events are indiscriminate and occur at all latitudes and in any lithology that happens to constitute the target material at the site of the impact. In this sense, impacts offer opportunities for many geochemical experiments in the origins of life. Although deep-ocean hydrothermal systems are not homogeneous and different chemical conditions are recognized in different vents (Russell & Arndt 2005), impact craters potentially offer a larger set of heterogeneous mineralogical conditions for prebiotic reactions, which might include early volcanic/granitic lithologies, nascent sedimentary lithologies and mixtures of different lithologies, where an impact occurs into a heterogeneous region or a region with a stratigraphic diversity.

During the period when the origin of life occurred, the diversity of rock types would have been much lower than today; the early crust was probably composed primarily of komatiites (Nisbet 1987). However, mobilization of minerals and their subsequent precipitation in the impact hydrothermal system would have locally enhanced the diversity of secondary minerals available for prebiotic reactions.

Perhaps, the most significant specific link between impact cratering and reactions for the origin of life are the formation of zeolites and clays as secondary minerals in impact hydrothermal systems. These minerals are formed by aqueous fluids that fill the heated rocks within the crater and react with the shock-derived aluminosilicates and impact glasses. Clays and zeolites offer charged ordered surfaces on which the sorption and oligomerization of reactants can occur, and they have been recognized as important potential templates for prebiotic reactions (Ferris *et al.* 1988; Zamaraev *et al.* 1997; Smith 1998; Saladino *et al.* 2001). The sorption and ion-exchange properties of clays and zeolites make them suitable both as sources and sinks for reactants.

The alteration minerals associated with post-impact hydrothermal systems have now been studied in at least 62 terrestrial impact structures. Altered minerals can contribute up to 25% of the mineralogy of the breccia formed in a crater. Most of the craters that have been studied show a great similarity in hydrothermal systems (Naumov 1996), with local variations caused by the target lithology. The most common hydrothermal minerals to be found are the assemblages of clay minerals including smectites with mixtures of zeolites and metal sulphides. On the early Earth, clay minerals would have been favoured in the subsurface, where the P_{CO_2} was reduced (Schoonen *et al.* 2004).

For example, in the Puchezh-Katunki crater, Russia, deep drilling elucidated the zonation of zeolites with Ca/Na and Al/Si ratios increasing downwards into the crater as the temperature of the mineral alterations increased (Naumov 1993). Laterally, the zeolites varied with zones of high-silica zeolites interspersed with low-silica varieties.

In the upper smectite-zeolite zone of Puchezh-Katunki crater, iron-bearing montmorillonites are to be found. High Fe-varieties of montmorillonite are found in the hydrothermal minerals of the Brent crater, Canada (Naumov 2005). Montmorillonites have received particular attention in studies of prebiotic

reactions. They can catalyse a wide diversity of prebiotic reactions (Ferris *et al.* 1988). The cationic surface of montmorillonite might provide template-directed synthesis of RNA oligomers (Paecht-Horowitz & Eirich 1988; Ferris & Ertem 1992, 1993; Ertem & Ferris 1996).

A diversity of other hydrothermal minerals found in craters has been shown to have significance for prebiotic chemistry. In many hydrothermal systems, such as those of Popigai crater, Russia; Carswell crater, Canada and Manson crater, USA, illite is to be found in the lithic breccias and melt rocks (suevite; Naumov 2005). Illite can act as a template for the synthesis of polypeptides (Hill *et al.* 1998; Liu & Orgel 1998; Orgel 1998). Ferris *et al.* (1996) synthesized polypeptides with over 55 monomers on illite clays.

With respect to early Earth, impacts into basalts may provide the closest analogous geochemical environments, just as organic formation in ultramafic deep-ocean hydrothermal systems (Holm & Charlou 2001) are recognized as potentially valuable analogues for early Earth. The 1.8 km diameter, 50 000-year-old Lonar crater, India, resulted from an impact, which occurred into the Deccan traps volcanic province. Hagerty & Newsom (2003) examined the hydrothermal minerals in this crater and found them to be dominated by saponite, formed optimally at temperatures between 130 and 200°C within the post-impact hydrothermal system. The ion-exchange properties of saponite minerals are well known (Breen & Moronta 2001) and potentially offer surfaces for the binding of organic molecules formed within the hydrothermal fluids.

These data suggest that within a single impact structure, a great diversity of organic-binding minerals with different characteristics can be formed, some of which may be more suitable than others as templates.

The production of other minerals, that are regarded as suitable surfaces for prebiotic reactions, is favoured in impact craters. Serpentinization can lead to the synthesis of double-layered hydroxides, compounds which act as ion-exchange surfaces (Cairns-Smith *et al.* 1992). The pore spaces of weathered feldspar have been previously suggested as environments conducive to prebiotic reactions on an account of the ion-exchange properties of this material (Parsons *et al.* 1998), which might concentrate organics, anions and cations. The impact-fractured surfaces of feldspar could act as surfaces for prebiotic reactions.

Impacts mobilize iron minerals, particularly transition metal sulphides, with potential consequences for prebiotic reactions (Cody *et al.* 2001; Cody 2004). Hydrothermal systems are known to precipitate metal sulphides; these minerals have been found in over 25 impact craters (Naumov 2005). The hydrothermal deposition of vast quantities of economically important metal-rich minerals in large impact structures such as Sudbury crater, Canada (iron-nickel ore; Ames *et al.* 1998) and Vredefort crater, South Africa (gold ore; Grieve & Masaitis 1994; table 1) attests to the role of impacts in the generation of minerals with significance for prebiotic reactions, and the correlation between crater size and quantity of minerals deposited. Large impacts on early Earth would have favoured mobilization of metal sulphides. The oxidative formation of pyrite (FeS_2) from

Table 1. Some characteristics of the impact craters discussed in this paper (ages are correct at the time of writing).

name	country	diameter (km)	age (Myr)
Brent	Canada	3.8	396 ± 20
Carswell	USA	39	115 ± 10
Charlevoix	USA	54	342 ± 15
Chesapeake	USA	90	35.5 ± 0.3
Haughton	Canada	24	23 ± 1
Kärdla	Estonia	7	~ 455
Lonar	India	1.83	0.052 ± 0.006
Manson	USA	35	73.8 ± 0.3
Popigai	Russia	100	35.7 ± 0.2
Puchezh-Katunki	Russia	80	167 ± 3
Ries	Germany	24	15.1 ± 0.1
Siljan	Sweden	52	361.0 ± 1.1
Sudbury	Canada	250	1850 ± 3
Tswaing	South Africa	1.13	0.220 ± 0.052
Vredefort	South Africa	300	2023 ± 4
Wolfe Creek	Australia	0.87	< 0.3

iron sulphide (FeS) is suggested as a chemoautotrophic pathway for early life (Wächtershäuser 1988, 1990). The mobilization of nickel and other metals in impact craters leads to the production of Fe–Ni sulphides and iron oxy-hydroxides, as at Sudbury crater, all of which are known to promote the reduction of simple precursors of organic molecules (Huber & Wächtershäuser 1997; Schoonen *et al.* 1999).

Impacts themselves may have delivered metallic Fe and Fe–Ni alloys to the surface of the Earth (Schoonen *et al.* 2004). Meteoritic iron has been shown to enable organic syntheses (Gelpi *et al.* 1970). These components of iron and iron–nickel meteorites would be entrained within the hydrothermal systems and melt-sheets of the impact structure created by the impactor itself, then the impact event may, in a very real way, catalyse its own prebiotic reactions.

(c) Available surfaces for reactions

A part of the kinetic energy of the impactor is manifest as shock waves, which alter the target lithology. At high shock pressures (approx. more than 50 GPa), rock melting can occur. Particularly in sedimentary lithologies, these high shock pressures can close pore spaces by both rearranging the grains and melting the material, which flows into the inter-grain space (Kieffer 1971; Kieffer *et al.* 1976). In these cases, we could expect that surfaces for prebiotic reactions would be decreased in abundance and accessibility. However, in a wide range of lithologies, impact-induced fracturing of the target rock occurs as a result of the propagation of shock waves. In many craters on Earth, an increase in fracturing in the target lithology has been empirically observed (e.g. Plado *et al.* 1996; Pesonen *et al.* 1999). This is usually expressed as a reduction in the density of the rock, an increase in porosity and permeability, and in some craters, an increase in ground conductivity, taken to reflect an increase in saline water within the fractured rock.

For a diversity of prebiotic reactions occurring on the surface of minerals, the number of sites for sorption

and ion exchange will be rate limiting (Schoonen *et al.* 2004). The likelihood of reactions occurring will be greatly improved by an increase in the surface area available. The impact-induced fracturing of rock vastly increases the surfaces available for reactions. In large craters, such as Siljan impact structure (52 km diameter), Sweden, the zone of fractured rock extends 5 km into the subsurface, and may exceed a volume of 1000 km³ (Naumov 2005). The fracturing of the rock in impact occurs concomitantly with the establishment of the post-impact hydrothermal system. In large areas of the crater, the fresh surfaces are immediately exposed to water circulation, and would provide abundant surfaces for sorption and ion exchange.

Oligomerization of the precursor molecules into more complex molecules, particularly self-replicating ones, is enhanced by non-random attachment of molecules to mineral surfaces and it has been shown to occur under simulated deep-ocean hydrothermal conditions (Imai *et al.* 1999). The likelihood of these processes can be increased by a large mineral surface area on which large numbers of oligomerization experiments can be accomplished, particularly if the reactions are inefficient (Orgel 1998). Large impact craters can offer many thousands of cubic kilometres of impact-fracturing rock in contact with hydrothermal systems for these reactions to occur. As fluids will be continuously recirculated by convection within an impact crater hydrothermal system, the surfaces will be refluxed with reactants and oligomerized products, leading to further oligomerization on the mineral surfaces, perhaps much more effectively than in deep-ocean hydrothermal systems, where the reactants are continuously being ejected into the dilute surrounding seawater.

A disadvantage of impact heated hydrothermal systems is the possibility of high salinities. The briny water in the deep subsurface of the Chesapeake impact structure, USA, has been attributed to hydrothermal evaporation during the Eocene impact (Sanford 2005). As high salt concentrations are unfavourable for the binding of reactants to mineral surfaces (Orgel 1998), regions of impact-induced high salinities, particularly where water becomes trapped and heated within a melt sheet, would be disadvantageous as regions for prebiotic chemistry. However, by contrast, fluid inclusion data from some craters suggest that the hydrothermal fluids of many craters have low (0–14% NaCl) salinities (Kirsimaë *et al.* 2002).

(d) Concentrating mechanisms

The concentration of reactants would occur within the hydrothermal system by virtue of deposition and sorption on the mineral surfaces with a supply of new reactants in hydrothermal fluids and confinement within the fractured rocks as explicated earlier. However, other concentrating mechanisms are possible. Near the surface of the crater, evaporative heating and drying of minerals, previously proposed as a concentrating mechanism (Usher 1977), would occur, but in this case induced by hydrothermal warming. This possibility conforms to the traditional notion of an evaporative pond as the location for the origin of life, suggested by Charles Darwin (1871).

In the case of continental impacts, the hydrologic depression formed by impact excavation will collect water, which subsequently evaporates and provides a concentrating mechanism. The salty playa in the Wolfe Creek impact crater, Australia, and the highly saline pond in the Tswaing impact crater, South Africa (both craters are *ca* 1 km in diameter), provide an empirical demonstration of the ability of crater depressions to act as sites for the collection and the evaporative concentration of fluids. If the majority of the Hadean continental crust was submerged, then these latter evaporative modes of concentration will be less important.

(e) *Appropriate physico-chemical conditions*

The fracturing, melting and redistribution of target rocks within a crater, both within the faults and within the melt sheet formed within and around the crater, can establish an astonishing diversity of geochemical gradients and juxtaposed physico-chemical conditions. It is recognized, for instance, that different mineral types offer particular advantages for the origin of life. Clays provide a surface for attachment and ion exchange, and Fe, Co, Cr and Cu-bearing minerals can provide catalysis for electron-transfer reactions and organic complexification (e.g. Foustoukos & Seyfried 2004). These minerals are not necessarily to be found in the same location. The fracturing and mixing of rocks prior to their re-emplacement within an impact structure can bring reactive surfaces into contact with one another, generating appropriate, and otherwise unusual, physical and chemical conditions over micro-metre scales.

The hydrothermal system can release catalytic metals from the target rocks, which then interact with templates to catalyse the prebiotic reactions. The hydrothermal release of iron has been demonstrated in the Charlevoix impact structure, Canada, where oxidized iron, together with aluminium and silicon, is found in the secondary minerals (Trepmann *et al.* 2005).

These diverse mineral assemblages might improve the chances of conditions favourable for oligomerization of early macromolecules. The mineralogical diversity has been suggested to provide a 'combinatorial library' of systems in which oligomerization could occur (Hill *et al.* 1998). As different amino acids and other precursors will adsorb onto different minerals with different affinities, depending on charge and local conditions (Liu & Orgel 1998), microenvironments that offer high geochemical diversity over small distances will provide environments in which potentially different and interacting oligomerization reactions might occur.

The establishment of thermal gradients within craters, which gives rise to the zonation of secondary minerals, will further lead to a diversity of physico-chemical conditions in the active hydrothermal system. We can thus think of the disrupted post-impact environment as a 'reactor' for prebiotic mineral surfaces.

Other chemical characteristics of post-impact hydrothermal systems lend themselves to prebiotic reactions. The impact hydrothermal systems typically have a pH of weakly alkaline to near-neutral pH (6–8)

and are supersaturated in silica (Naumov 2005). These pH values are compatible with several of the prebiotic reactions described by Wächtershäuser (1990). In Wächtershäuser's scheme, the pH values must be suitable to allow for high concentrations of HS[−], corresponding to pH values greater than 4.5. Many of his cleavage reactions are also favoured by non-acidic pH values. The non-acidic pH is generally more suitable for the surface binding of organics to cationic minerals, and the preservation of organic material, for any prebiotic reaction sequence. Acidic conditions are not precluded in impact-induced hydrothermal systems. Osinski *et al.* (2001) suggest that one explanation for marcasite deposition in the hydrothermal systems of the Haughton crater, Canada, would be reduction of the pH of the hydrothermal system to below 5. However, geochemical evidence suggests that neutral or alkaline pH values are usual for post-impact hydrothermal systems (Naumov 2005).

By contrast, deep-ocean hydrothermal systems exhibit a diversity of fluid pH values; many of them are acidic, but some exhibit highly alkaline conditions (Russell & Arndt 2005), which may themselves inhibit prebiotic reactions.

(f) *Longevity of conditions and effects of cooling*

There is no constraint on the length of time required for the origin of life. An important difference between deep-ocean hydrothermal systems and impact-generated hydrothermal systems is the comparatively temporary nature of the latter. The larger the impact structure, the more long-lived the hydrothermal system will be. For example, at the 24 km diameter Haughton impact structure in Canada, the mineralogical data has been interpreted to suggest a hydrothermal system lasting *ca* 10 000 years (Osinski *et al.* 2001). Versh *et al.* (2003) estimated that the hydrothermal system in the 4 km diameter Kärđla crater, Estonia, lasted for several thousand years, and Abramov & Kring (2004) suggest a lifetime of over 2 Myr for the hydrothermal system in the 250 km diameter Sudbury impact structure, Canada.

The impact hydrothermal systems start at much higher temperatures than deep-ocean hydrothermal systems. The initial temperature of the Haughton crater hydrothermal system has been estimated at *ca* 650–700°C (Osinski *et al.* 2001). Similarly, the Ries crater (Germany) hydrothermal system may have sustained similar temperatures during emplacement (Pohl *et al.* 1988). By contrast, on-axis hydrothermal systems, which achieve the highest temperatures of deep-ocean hydrothermal systems, emanate water temperatures of typically 350–370°C. Thus, impact-induced hydrothermal systems will host a potentially much larger diversity of mineral deposition sequences.

The relatively short duration of impact hydrothermal systems, compared to deep-ocean vents, may appear to constrain the opportunity for the origin of life. However, as hydrothermal systems cool, more complex molecules can form as lower temperatures favour their stability (Shock & Schulte 1998). In contrast to deep-ocean hydrothermal vents, the general cooling trend within impact structures creates conditions, whereby over the lifetime of the hydrothermal

system, a large diversity of thermal and cooling regimens are 'tested', which potentially corresponds to a large diversity of organic syntheses conditions.

In a diversity of simulated experiments to test organic synthesis in hydrothermal conditions, too numerous to adequately review here (e.g. Marshall 1994; Imai *et al.* 1999; McCollom *et al.* 1999; Ogasawara *et al.* 2000), it is apparent that different temperatures favour different syntheses. For example, in simulated laboratory hydrothermal experiments run between 100 and 400°C in stainless steel vessels using oxalic and formic acid as reactants (as a proxy for H₂, CO and CO₂), Rushdi & Simoneit (2001) showed that alkanolic acids were optimally formed at 300°C and alkyl formates at the lower temperature of 200°C. Other compounds showed distinctive temperature optima.

Theoretical studies also show that different organic syntheses will be reached at defined temperature optima. The formation of many organic compounds in modelled hydrothermal systems is optimal at temperatures of 150–250°C (Shock 1990, 1992) and the products of these syntheses, such as acetate, are generally optimally stable at similar or lower temperatures (Mottl 1992). Thus, any geothermal environment that allows for temperature variations from several hundred degrees to much lower temperatures, will potentially maximize the diversity of organic syntheses.

As the rate of cooling of impact-induced hydrothermal systems will vary from hours to millions of years, depending on the scale of impact, the target lithology and the nature of convective fluid flow, this will further add to the diversity of chemical conditions tested on Hadean Earth. The optimum conditions for different reactions will be reached at different times, but in the same locations, as the cooling of the hydrothermal system brings the crater through the metastable equilibria of aqueous organic compounds. Thus, hydrothermal cooling may even allow for a type of 'temporal' compartmentalization of the reaction sequences in the prebiotic period, when cellular compartmentalization was not available.

By contrast, on-axis deep-ocean hydrothermal systems have water temperatures much higher than those optimum for organic syntheses. As a result, environments for prebiotic synthesis have focused more on flank hydrothermal systems (Holm 1992), where temperatures are more typically *ca* 150°C. The more constant temperature regimens would limit the opportunity for diverse reaction sequences in a single location, although temperatures will clearly vary over spatial scales, but then any mineral-bound reaction products will be separated from other reaction products produced at different temperatures.

(g) *Environment for the emergence of life from the prebiotic reactions*

Whatever conditions we postulate for prebiotic reactions, they must be compatible with early life, in the sense that the end product of the prebiotic reactions is a proto-micro-organism that must be capable of survival, and growth, in the conditions that gave rise to it. Both the deep-ocean hydrothermal vents and the impact-induced hydrothermal systems offer environments suitable for thermophilic and hyperthermophilic

life. In the case of impact structures, unlike deep-ocean hydrothermal vents, there is no fresh crater existing today in which to directly observe the colonization of post-impact hydrothermal systems by extant micro-organisms, but by analogy, we can infer that impact-induced hydrothermal systems, when cooled to below the upper temperature limit for life, would have offered environments for early life (Koeberl & Reimold 2004).

3. A SCHEME FOR THE ORIGIN OF LIFE WITHIN IMPACT CRATERS

A tentative scheme for the origin of life within Hadean impact structures can be proposed. During the collision of the asteroid or comet into the oceans or exposed land masses, rocks are heavily shocked and fractured in large volumes of the target material. A thermal anomaly is generated from the kinetic energy of the object. A hydrothermal system is established within and around the crater, and secondary mineral deposition starts to occur. At high temperatures, potentially catalytic metals are released from the target rock and deposited within metal pyrites, and zeolites and clays are laid down within the hydrothermal veins and fractured rocks.

As the crater begins to cool to temperatures in the range 50–250°C, several pathways to organic complexification occur. The presence of CO₂ and H₂ (from the Hadean atmosphere)—H₂ being augmented by deep impact-fracturing of Hadean basalts in contact with seawater, resulting in serpentinization and localized formation of H₂—would provide the raw material for organic synthesis as the hydrothermal fluids come into contact with seawater or fluids within the crater at different temperatures. Alternatively, the reduction of CO₂ could occur in the fluids by catalytic action as it comes into contact with precipitated iron–nickel hydrothermal minerals in the presence of H₂ in the scheme proposed by Russell *et al.* (1998) and empirically shown to be capable of producing CH₄ under simulated hydrothermal conditions by Horita & Berndt (1999), or in contact with ferrous sulphide and hydrogen sulphide in the schemes proposed by Wächtershäuser (1988, 1990). Some of these Fe–Ni reaction sites may be part of iron–nickel impactors themselves and incorporated within the impact breccia and suevites. Some organics may already be present in the system, generated by shock synthesis during the impact itself and some organics would be present as material delivered by earlier impactors during this period of heavy bombardment.

Hydrothermal cooling drove the crater environment through temperature optima for a vast diversity of organic syntheses and complexification reactions. In some craters, the cooling was too quick for syntheses to produce enough product for subsequent reactions, whereas in some it was too slow so that reactants from one synthesis were no longer available for later syntheses; but in some craters where the kinetic energy deposited into the target lithology was just right and the cooling caused by convection and local conditions was optimal, the organic syntheses of various types would have occurred with optimal rates.

Figure 1. Darwin's warm little pond—the impact crater as a prebiotic reactor. Some of the diversity of characteristics of impact structures that make them favourable sites for prebiotic reactions are shown.

Figure 2. Impact craters as a habitat. Some of the characteristics of impact craters that make them favourable sites for microorganisms are shown.

The production of organics proceeded to more complex stages through the schemes proposed by Russell and Wächtershäuser and others within the clusters of iron minerals (e.g. pyrite, greigite and mackinawite) laid down within the hydrothermal systems of the crater. As the crater hydrothermal system cooled to temperatures *ca* 40–100°C, the organic synthesis of acetate, according to the scheme demonstrated by Huber & Wächtershäuser (1997) and also the scheme suggested by Russell, would have been favourable.

Equally plausible, at least from the point of view of the available geochemical environment, is that organics generated from the various mechanisms available, and described earlier, bound to the impact-generated zeolites and clays within the crater. During crater cooling, oligomerization reactions were favoured during the hydrothermal circulation, with the products

of one clay/zeolitic reaction being transferred to other templates during circulation, resulting in the 'testing' of many oligomerization experiments in diverse physico-chemical conditions, and on diverse substrates throughout the crater.

Hydrothermal cooling favoured the emergence of more labile complex molecules (Shock & Schulte 1998) and at some point within the crater history temperatures dropped to conditions favourable for complex nucleic acids, cell membranes and other proto-cellular structures (e.g. Tsukahara *et al.* 2002) required for the emergence of self-replicating systems.

Finally, and more speculatively, it is worth noting that these same prebiotic processes may have occurred in Martian impact craters. Limited tectonic activity on early Mars may have significantly constrained the possibility for deep-ocean type hydrothermal systems.

Impact-induced hydrothermal systems may have been the only means to have generated sustained hydrothermal systems for prebiotic reactions.

A schematic of the processes occurring in a crater is shown in figure 1.

4. CRATERS AS HABITATS FOR EARLY LIFE

Asteroid and comet impact craters offer some advantages to lithophytic organisms (Cockell *et al.* 2005; figure 2), and on early Earth, these environments would have provided suitable places for the proliferation and radiation of life (Cockell 2004) once it did emerge. The fracturing of rock during impact will greatly increase the surface area available for microbial colonization, although nutrient limitation could limit the degree to which such void space can actually be used (Cockell *et al.* 2005), particularly in the subsurface.

During the early post-impact phase, the crater offers an environment for what we have previously termed the 'phase of thermal biology', defined as that phase 'during which the thermal anomaly associated with a recently formed crater sustains biological activity of a nature or at a level requiring warmer environmental conditions than would be available in the same area had the impact event not occurred' (*sensu* Cockell & Lee 2002). As adumbrated by Naumov (2005), in most post-impact hydrothermal environments, these warmer conditions would be accompanied by neutral to alkaline pH values, favouring neutrophilic and alkalinophilic organisms, although localized regions of acid conditions are not implausible. The metabolic characteristics of these communities might be analogous to those that inhabit deep-ocean hydrothermal systems today (e.g. Nercessian *et al.* 2003; Alain *et al.* 2004). As there is no fresh crater available for study, the true nature of the hydrothermal microbial ecosystems that inhabited early Archaean craters must be subject to some conjecture, but if the earliest life forms were hyperthermophilic, perhaps owing to an evolutionary bottleneck, then impacts would not only have caused this bottleneck, but also would have generated hot conditions that favoured colonization by the microorganisms that survived the previous impacts.

The impact-shocked crystalline rocks can provide cryptoendolithic environments for diverse organisms. We have previously shown how, by both increasing porosity and light transmission, impacts can generate novel habitats for photosynthetic micro-organisms (Cockell *et al.* 2002). Habitats within rocks for phototrophs are otherwise limited to porous sedimentary lithologies or macroscopic cracks in rocks (chasmoendolithic communities) on the present-day Earth. The presence of photosynthetic organisms on the early Archaean Earth is somewhat equivocal, but impact-shocked rocks will equally provide a refugium for heterotrophs and chemolithotrophs, perhaps aiding escape from a putatively harsh UV radiation regimen (Cockell 2004; Cockell & Lim 2005). The minerals laid down by impact hydrothermal systems can provide sites for microbial colonization. Microbial colonization of selenite within the Haughton impact structure has been demonstrated (Parnell *et al.* 2004).

Figure 3. Organisms associated with impact melt sheets (suevites) in the Haughton impact structure, Canada. (a) A biofilm of organisms associated with a cavity inside the material (scale bar 0.1 mm); (b) microfungi associated with the biofilms (scale bar 30 µm); (c) the diverse mineralogy of the breccia (granites, dolomite, gneiss, sandstones) provides a geochemically diverse environment for microorganisms (scale bar 0.3 mm)

Micro-organisms will also colonize suevites and lithic breccias. Impact events shatter and mix target rocks. Some are thrown from the crater, but a considerable volume of fall-back breccias and suevites are deposited within the excavation cavity itself. Upon cooling to temperatures favourable for life, the resulting material contains diverse geochemical interfaces between lithologies that may not otherwise be in contact with each other. In the Haughton impact structure, Canada, we have observed the presence of filamentous micro-organisms (presumptive fungi) at the interface between mudrock emplaced within the suevite and the silicate-carbonate melt that comprises the matrix (C. Cockell, J. Watson, unpublished data; figure 3). The material has sufficient porosity to allow for the movement of micro-organisms into the rock matrix.

On early Earth, mixing of lithologies in this way would have distributed minerals and established geochemical gradients (albeit with the probably more limited mineralogy available on early Earth compared to present-day Earth), which would have provided diverse redox couples for micro-organisms to conserve energy for growth. Further, geochemical gradients would be established between the mixed rocks and the secondary minerals deposited on their surfaces during hydrothermal circulation in the heavily fractured rocks.

5. CONCLUSION

Favourable conditions for the origin of life require that a diversity of factors come together in a single location. Asteroid and comet impact craters offer favourable conditions for prebiotic reactions that are an amalgam of conditions, which have previously been postulated as required for the origin of life. The origin of life in the post-impact environment is not an alternative to existing theories, but rather offers an expansion of the possible number of favourable environments in which such experiments may have occurred. The environments described in this paper apply to both hydrothermal systems on early cratons and those established on the seabed following impact into the Hadean oceans. The chemical and the physical conditions, which arise in and around impact craters, suggest that Charles Darwin's 'warm little pond' (Darwin 1871) has literal relevance in understanding possible environments for the origin of life, and not merely the metaphorical meaning to which it has, in recent times, been relegated.

After the origin of life, up to the present day, impact craters offer favourable environments for colonization by lithophytic organisms. Craters offer a localized source of liquid water, mobilization of minerals and carbon and, in melt sheets and suevite, a potentially large diversity of geochemical gradients, particularly where the lithologic target sequence is diverse, subaerial and submerged craters would have offered favourable environments for diverse microbial communities on early Earth.

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Discussion

J. I. Lunine (*Lunar and Planetary Sciences Department, University of Arizona, USA*). Your excellent treatment of terrestrial hydrothermal systems can be extended to environments on Mars and Saturn's Moon Titan as well. On Mars, the abundant impact craters in crust that holds water ice might create transient liquid water environments, where prebiotic chemistry could be hosted perhaps through to the origin of life. On Titan, impacts into the organic bearing water ice crust would have provided liquid water for hundreds or thousands of years, in which the organic molecules might have undergone interesting prebiotic reactions. There's a beautiful 450 km diameter crater captured by Cassini radar on Titan that shows evidence for reworking, channels and possibly infill or flooding. It is a candidate for a return mission to Titan.

This is correct that impact hydrothermal systems may be places for complex organic chemistry on other planets and indeed there has been some work in this direction already. Of course, if the hydrothermal systems produce complex organic compounds, then they are very interesting, but much less interesting if the opportunity is not there for the emergence of life following the complexification of the organics.

C. S. Cockell. I should say that in the context of applying these ideas to other planets, it is the case that owing to the lack of, or the short duration of, plate tectonics on Mars, or indeed, any Mars-like planet elsewhere, where deep-ocean hydrothermal systems at spreading centres may not exist, then impact-induced hydrothermal systems may be even more important as sites for these early reactions, maybe even the only sites. I focused my discussion on Earth owing to the focus of the discussion meeting, but your comments on the relevance of these discussions to other planets are very valuable.

F. Diego (*Department of Physics and Astronomy, University College London, London, UK*). Can you comment on the conditions in tidal basins compared

to hydrothermal vents in deep sea and impact craters as environments for emergence of life. How do these environments compare to each other? Does life need high temperature only present in hydrothermal vents, but NOT in tidal basin ponds?

C. S. Cockell. Tidal basins have always been a favoured location for the origin of life. We obviously do not know whether the origin of life needed high temperatures, but high temperatures do provide favourable conditions for organic syntheses (assuming these were required endogenously) and for speeding up organic reactions (although not too hot or high temperatures will break down organic compounds). Tidal pools offer the advantage of possible evaporative concentration of reactants on mineral surfaces or just in solution, although one can imagine concentration of reactants in hydrothermal veins as they become attached to mineral surfaces. To evade your question—yes, each environment does have some advantages and disadvantages, but I think we just do not know enough about the origin of life to be able to say 'this environment is much more likely than another'.

F. Diego. Why is the temperature decay after the impact so slow; i.e. from 500 to 100°C in as long as 10 000 years?

C. S. Cockell. The decay of temperature obviously depends on the scale of the impact. Remember that the kinetic energy squares with the velocity and these objects are coming in at over 10 km s⁻¹. That is a lot of energy delivered into the bed rock. The rate of cooling will be influenced by convection, the local climate and many other factors. However, that time period of 10 000 years is estimated for a crater of about 25 km across. Larger craters such as Sudbury, which is over 200 km across, would potentially drive hydrothermal systems for over a million years. It seems slow, but that's quite quick geologically and the question is, of course, is such a time period too quick to be useful for the origin of life?