Catalytic peptide hydrolysis by mineral surface: Implications for prebiotic chemistry

Karina Marshall-Bowman [a], Shohei Ohara [b], Dimitri A. Sverjensky [b,c], Robert M. Hazen [b], H. James Cleaves [b,*]

[a] University of Vermont, Burlington, VT 05401, USA
[b] Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA
[c] Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA

Abstract

The abiotic polymerization of amino acids may have been important for the origin of life, as peptides may have been components of the first self-replicating systems. Though amino acid concentrations in the primitive oceans may have been too dilute for significant oligomerization to occur, mineral surface adsorption may have provided a concentration mechanism. As unactivated amino acid polymerization is thermodynamically unfavorable and kinetically slow in aqueous solution, we studied mainly the reverse reaction of polymer degradation to measure the impact of mineral surface catalysis on peptide bonds.

Aqueous glycine (G), diglycine (GG), diketopiperazine (DKP), and triglycine (GGG) were reacted with minerals (calcite, hematite, montmorillonite, pyrite, rutile, or amorphous silica) in the presence of 0.05 M, pH 8.1, $KHCO_3$ buffer and 0.1 M NaCl as background electrolyte in a thermostatted oven at 25, 50 or 70 °C. Below 70 °C, reaction kinetics were too sluggish to detect catalytic activity over amenable laboratory time-scales. Minerals were not found to have measurable effects on the degradation or elongation of G, GG or DKP at 70 °C in solution. At 70 °C pyrite was the most catalytic mineral with detectible effects on the degradation of GGG, although several others also displayed catalytic behavior. GGG degraded ∼1.5–4 times faster in the presence of pyrite than in control reactions, depending on the ratio of solution concentration to mineral surface area. The rate of pyrite catalysis of GGG hydrolysis was found to be saturable, suggesting the presence of discrete catalytic sites on the mineral surface. The mineral-catalyzed degradation of GGG appears to occur via a GGG → DKP + G mechanism, rather than via GGG → GG + G, as in solution-phase reactions. These results are compatible with many previous findings and suggest that minerals may have assisted in peptide synthesis in certain geological settings, specifically by speeding the approach to equilibrium in environments where amino acids were already highly concentrated, but that minerals may not significantly alter the expected solution-phase equilibria. Thus the abiotic synthesis of long peptides may have required activating agents, dry heating at higher temperatures, or some form of phase separation.
© 2010 Elsevier Ltd. All rights reserved.

1. INTRODUCTION

It is generally believed that organic polymer formation may have been important for the origin of life (Miller and Orgel, 1974). The relevant types of environments and the organic molecules contributing to the origin of life remain open questions (Cleaves and Lazcano, 2009): many posit specific geochemical settings, for example shallow evaporitic or hydrothermal environments. The onset of plate tectonics, weathering, erosion and sedimentation likely produced a variety of microenvironments where life may have arisen (Lahav and Chang, 1976; Chang, 1988).

Many models for the origin of life hold that polypeptides were essential for the first living systems (Fox and

---

Harada, 1958; Kauffman, 1971; Wächtershäuser, 1988; Russell and Hall, 1997; De Duve, 2003; Ikehara, 2009). Amino acids are central to such schemes and it seems reasonable that they were available on the early Earth via a variety of sources (Miller, 1953, 1955; Stribling and Miller, 1987; Chyba and Sagan, 1992; Cleaves and Lazcano, 2009).

A significant problem with peptide-based models for the origin of life is that the prebiotic oceans would likely have been extremely dilute with respect to amino acid concentrations (Miller and Orgel, 1974; Stribling and Miller, 1987; Aubrey et al., 2009; Cleaves et al., 2009). The concentration of amino acids in the primitive ocean has been estimated variously from 4×10^{-3} M (Stribling and Miller, 1987) to 10^{-7} M (Lahav and Chang, 1976). While modern biochemical peptide synthesis depends on informationally directed mechanisms that use high-energy activated monomers for the synthesis of peptides, in the pre-life era, high concentrations of amino acids would have been required for unactivated peptide polymerization to occur (Lahav and Chang, 1976).

Bernal proposed that mineral surface adsorption could have helped to overcome this problem (Bernal, 1951). Chang (1988) surveyed the potential of mineral surfaces to adsorb dilute monomers, and concluded that it was unlikely that this was the case. However, there are also more recent experiments that suggest that some amino acids are adsorbed very strongly to some mineral surfaces, especially under appropriate conditions of pH and ionic strength (Sverjensky et al., 2008; Jonsson et al., 2009, 2010; Hazen and Sverjensky, 2010). Understanding the possible contributions of mineral surfaces to peptide oligomerization is thus central to several models for the origin of life (Orgel, 1998; Zaia, 2004). Mineral adsorption could have facilitated peptide formation by increasing the effective concentration at the mineral surface and/or by providing catalytic sites on the surface (Lahav and Chang, 1976; Wächtershäuser, 1988; Russell and Hall, 1997; Rode et al., 1999).

Minerals such as silicates, oxides and sulfides were likely present on the early Earth in various environments (Schoonen et al., 2004; Hazen et al., 2008; Lambert, 2008). Clays and other fine grained sedimentary minerals may have provided the most likely surface for adsorption and condensation of amino acids owing to their high specific surface area (Ponnamperuma et al., 1982; Porter et al., 1998). Although many previous studies have examined the effects of minerals on peptide elongation in evaporative environments (Fox and Harada, 1958; Dose, 1983; Rode et al., 1999; Plankensteiner et al., 2004), as well in the presence of various condensing agents (Chang et al., 1969; Hawker and Oró, 1981; Hill et al., 1998; Liu and Orgel, 1998a,b; Leman et al., 2004), few studies have examined the catalytic effects of mineral surfaces on unactivated aqueous peptide oligomerization or degradation.

Direct condensation of amino acids to peptides in aqueous solution is thermodynamically unfavorable. The free energy of hydrolysis of a peptide bond is estimated by numerous authors as ~ 3.5 kcal/mol (Dobry et al., 1952; Meggy, 1956; Flegmann and Scholefield, 1978; Flegmann and Tattersall, 1979; Kahne and Still, 1988; Martin,

1998), corresponding to an equilibrium of dipeptide in a concentrated 1 M amino acid solution of $\sim 2.7 \times 10^{-3}$, 5.9×10^{-3} and 3.5×10^{-2} M at 25, 70, or 250 °C, respectively, assuming no monomer degradation. It should be noted that if all of the nitrogen in the present atmosphere were dissolved in oceans of the present size in the form of glycine, the concentration would be ~ 1 M (Schwartz, 1981). At the high end estimate of geochemically plausible amino acid concentration (3×10^{-4} M, as discussed above), the equilibrium dipeptide concentrations are 2.4×10^{-10}, 5.3×10^{-10} and 3.1×10^{-9} M at 25, 70 or 250 °C, respectively, again assuming no degradation of monomer. While monomer/polymer equilibrium is more favorable at higher temperatures, monomer decomposition (White, 1984; Qian et al., 1993; Bada et al., 1995) rapidly draws the reaction back towards net depolymerization at high temperatures (Cleaves et al., 2009).

An important point to bear in mind is the nature of mineral catalysis. Strictly speaking, a catalyst is a substance that lowers the activation energy of a reaction but that is not itself consumed in the reaction. The lowering of the activation energy of a reaction, by the principle of microscopic reversibility, increases the rates of both the forward and reverse reactions, and thus increases the rate of approach to thermodynamic equilibrium. If surfaces act as true catalysts, then they should facilitate the approach to equilibrium from both directions, thus they should also facilitate peptide hydrolysis, potentially offering no advantage to oligomerization, only a more rapid arrival at the thermodynamically determined equilibrium. Interestingly though, they could speed the attainment of equilibrium at lower temperatures, especially in evaporative environments.

We chose to work with glycine because it is achiral and therefore stereochemistry and racemization can be ignored, and it is one of the most abundantly produced prebiotic amino acids (Miller, 1953, 1955; Oró and Kamat, 1961; Lowe et al., 1963; Kvenvolden et al., 1970; Marshall, 1994; Johnson et al., 2008; Elsila et al., 2009). Glycine is also one of the most chemically stable α-amino acids (Abelson, 1959; Vallentyne, 1964; Hare and Mitterer, 1969; Andersson and Holm, 2000; Snider and Wolfenden, 2000; Li and Brill, 2003a,b) and therefore the conclusions reached may be true of many amino acids (Cleaves et al., 2009). However, it is also clear that some amino acids, for example those with multiple negative or positive charges, such as aspartic and glutamic acids and lysine may form inner-sphere complexes with oppositely charged mineral surface sites mediated via their ionizable side chains (Sverjensky et al., 2008; Jonsson et al., 2009, 2010), which may be bound considerably more strongly than those formed by simple zwitterions like glycine. There may thus be significant differences between peptides composed of more complex charged amino acids and oligoglycines. This effect will be the topic of a future investigation.

Despite glycine's structural simplicity, its aqueous chemistry is quite complex (Fig. 1). For example, in addition to various modes of decomposition (principally to glycolic acid and ammonia, or methylamine and CO_2 (Aubrey et al., 2009; Faisal et al., 2008), glycine can condense to give a dimer, glycylglycine (GG). The dimer can then
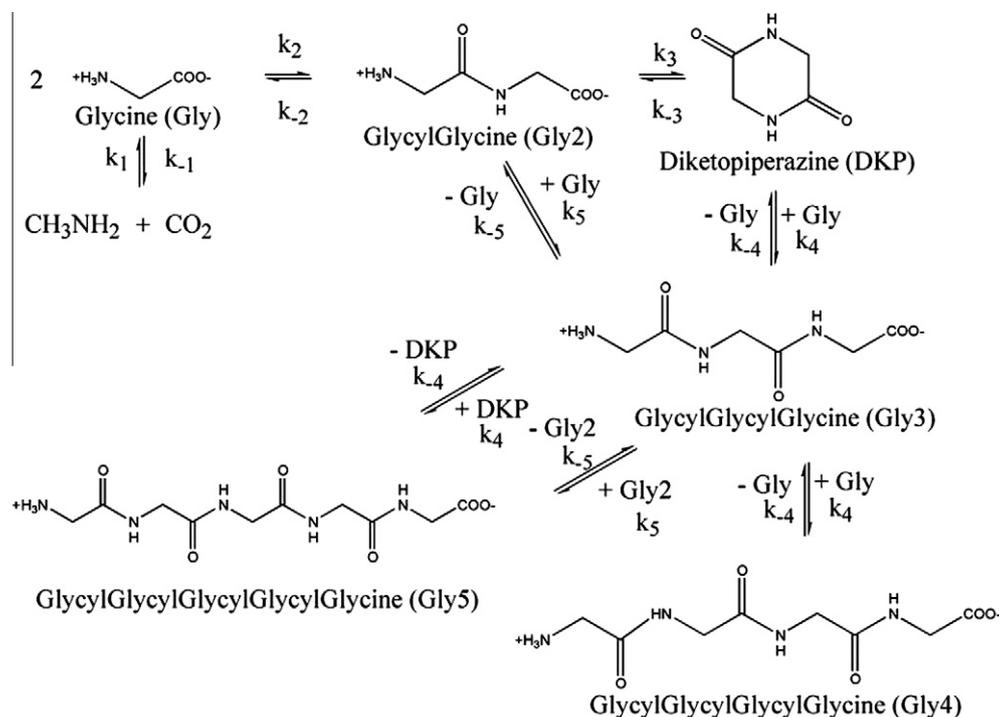
Fig. 1. Some possible aqueous oligomerization and degradation pathways for glycine and its higher oligomers.

cyclize to yield the cyclic dimer 2,5-diketopiperazine (DKP) (Radzicka and Wolfenden, 1996; Li and Brill, 2003c). Glycine and its oligomers can lengthen reversibly via addition of monomers or higher peptides (Martin, 1998; Cleaves et al., 2009), or via a ring-opening polymerization involving DKP (Meggy, 1953; Kozai et al., 1975; Nagayama et al., 1990). The hydrolysis of polypeptides can occur via direct peptide scission or via a more rapid "tail-biting" mechanism which generates a peptide two amino acid residues shorter and a DKP.

2. MATERIALS AND METHODS

All chemicals were purchased from Sigma–Aldrich. Minerals were obtained from various sources as shown in Table 1. The specific surface areas of the minerals were measured by BET multipoint isotherm analysis by Micromeritics (Norcross, Georgia). These values and other physical properties of the minerals tested are shown in Table 1.

The purity of the minerals was also assayed using scanning electron microscopy (SEM) using back-scattered electron (BSE) imaging and energy-dispersive spectroscopy (EDS) performed on a JEOL JSM 6500F scanning electron microscope with a field emission gun equipped with a liquid N_2-cooled sapphire Si(Li) EDS detector (EDAX) using a 15 kV operating voltage.

Reactions were carried out under air in 15 mL polystyrene Falcon tubes or 1.5 mL gasketed Eppendorf tubes. Experiments were typically conducted using 100 mg of mineral with 10 mL of a solution containing 0.001 M glycine

Table 1
Properties of the minerals used in this study.

Mineral	Formula	Source	Particle diameter (μm)	BET surface area (m²/g)	pH$_{pzc}$	Purity (%)
Pyrite	FeS_2	1	43–74	0.562 ± 0.004	1.7[a]	95[b]
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$	2	~5	24.34 ± 0.116	~6.5	>99
Calcite	$CaCO_3$	3	43–74	0.389 ± 0.002	9.5[c]	>99
Rutile	TiO_2	4	<5	2.485 ± 0.009	~4.3[d]	>99
Hematite	Fe_2O_3	4	<5	4.991 ± 0.007	4.3–9.0[e]	>99
Silica	SiO_2	4	75–150	480	~3.5	≥99

Notes: (1) Huanzala, Peru; (2) SAz-1, The Clay Minerals Society, West Lafayette, IN (clay from Apache County, AZ); (3) Carthage Mine, Elmwood, Tennessee; (4) Sigma–Aldrich.
[a] Weerasooriy and Tobschall (2005).
[b] Five percent unidentified silicate contaminant.
[c] Churchill et al. (2004).
[d] Measured directly by potentiometric titration.
[e] Parks (1965).

derivative, 0.05 M KHCO$_3$ (pH 8.1) and 0.1 M NaCl. Control reactions were also carried out in the absence of minerals. It is known that carbonate species adsorb to the surfaces of many minerals, and there may thus be competition for adsorption. Nevertheless, natural aquatic systems typically contain significant concentrations of carbonate species.

A pH 8 was chosen as it is roughly the pH of the modern ocean, and this value may have been fairly constant over time (Abelson, 1966; Sillén, 1967; Grotzinger and Kasting, 1993), although there are dissenting models for the pH of the bulk Archaean ocean ranging from pH 5.5 to 10.5 (Russell and Hall, 1997; Morse and Mackenzie, 1998; Kempe and Kazmierczak, 2002). It is of course also possible that various microenvironments existed on the primitive Earth with widely varying pH values. Tubes were placed on a rotator to ensure efficient mixing of the reactions. The rotator was inserted into a drying oven, which allowed for constant control of the reaction temperature ±∼1 °C as monitored with a mercury thermometer. Reactions were conducted at room temperature (∼25 °C), 50, 70 and 100 °C to investigate the effects of temperature on the reaction kinetics. Samples were withdrawn after ∼30, 60, 90 and 120 h. Glycine oligomers (gly1–gly6) and DKP were analyzed according to the procedure of Imai et al. (1999) using an HP 1050 HPLC system with UV detection at 210 nm with a Phenomenex 150 × 4.6 mm C-18 column eluted with, pH 2.5, 50 mM KH$_2$PO$_4$ containing 7.2 mM sodium hexane sulfonate at a flow rate of 0.5 mL/min. Injection volume was 50 μL.

The detection limits of the HPLC analysis was ∼10^{-6} M for G, GG, DKP and GGG, respectively. Standards from glycine up to hexaglycine were chromatographed to determine retention times and to generate standard curves. Due to the increasing number of amide bonds per molecule, the UV extinction coefficients increase, and thus the detection limits for higher peptides also increase. The identities of the products were also confirmed by LC–MS. LC–ESI-MS analyses were carried out using an ACQUITY UPLC system with a Waters ACQUITY UPLC HSS T3 (1.8 μm, 2.1 × 150 mm) column, using 5 mM undecafluorohexanoic acid as the mobile phase at a flow rate of 0.2 mL/min at 40 °C. The injection volume was 5 μL.

3. RESULTS AND DISCUSSION

3.1. Adsorption

Typical of many organic compounds, oligoglycine adsorption strength generally increase as molecular weight increases (Greenland et al., 1962, 1965; Basiuk et al., 1995; Basiuk and Gromovoy, 1996; Zhou et al., 2001) (although there are exceptions, see for example Dashman and Stotzky, 1984), and as has been pointed out it may be difficult to differentiate between oligomerization, degradation and adsorption (Lambert, 2008). Using the measured specific surface areas of the minerals studied (Table 1) and assuming molecular cross-sections of 16, 30, 25 and 45 Å^2 for glycine, GG, DKP and GGG, respectively, and assuming monolayer adsorption, the maximum number of moles that could have been adsorbed on each mineral are shown in Table 2.

As can be seen, except in the case of silica, since each reaction typically contains ∼10^{-4} mole of amino acid derivative, less than 10% of the amino acid derivatives could be adsorbed at maximum surface coverage. The surface area of the silica is high enough, however, that all of the organic species could potentially be adsorbed. However, we found a near complete mass balance of the input species in the solution phase in all of the reactions studied, within experimental error.

3.2. Effect of temperature

Glycine peptide hydrolysis was too slow to be measurable at 25 and 50 °C. 100 °C also proved to be experimentally complicated due to mechanical failure of the plastic sample tubes. 70 °C was found to be a good compromise. This is coincidentally a temperature characteristic of many low temperature off-axis hydrothermal vent environments such as Lost City (Kelley et al., 2005), and is similar to some estimates for mean early Archean ocean temperatures (Knauth and Lowe, 2003).

3.3. Effect of concentration

Reactions were studied at various initial reactant concentrations, from 0.1 to 10^{-4} M. Kinetics were generally comparable at all concentrations at 70 °C and lower. As noted above, 0.001 M is likely higher than the estimated prebiotic bulk oceanic concentration of amino acids, but allowed for convenient analysis of reactions within the dynamic range of the analytical methods.

3.4. Glycine

No peptides were detectable from 0.1 M glycine (or lower concentrations) at 70 °C after 1 week with any mineral, which agrees well with the thermodynamic analysis

Table 2
Potential number of moles of glycine derivatives adsorbed to the mineral surfaces studied assuming a monolayer adsorbed.

Mineral	Surface area/reaction (m^2)	Glycine	GG	DKP	GGG
Pyrite	0.56	5.6×10^{-7}	3.0×10^{-7}	3.6×10^{-7}	2.0×10^{-7}
Montmorillonite	2.43	2.5×10^{-5}	1.3×10^{-5}	1.6×10^{-5}	8.7×10^{-6}
Calcite	0.39	3.9×10^{-7}	2.1×10^{-7}	2.5×10^{-7}	1.4×10^{-7}
Rutile	2.49	2.5×10^{-6}	1.3×10^{-6}	1.6×10^{-6}	8.9×10^{-7}
Hematite	4.99	5.0×10^{-6}	2.7×10^{-6}	3.2×10^{-6}	1.8×10^{-6}
Silica	48.0	4.8×10^{-4}	2.6×10^{-4}	3.1×10^{-4}	1.7×10^{-4}

presented above, and our estimated detection limits for peptides.

3.5. Glycylglycine

At 70 °C and below and a concentration of 0.1 M and below, all minerals tested had decomposition curves comparable to the control for GG after 1 week of reaction. No elongation was detected in any of the reactions, and no cyclization or hydrolytic catalysis over the control reactions was noted.

3.6. Diketopiperazine

No observable increase in the rate of ring opening or peptide hydrolysis was noted over the control reactions with any of the minerals tested using 0.1 M or lower concentrations of DKP at 70 °C and below.

3.7. Glycylglycylgylcine

A plot of the natural logarithm of the GGG concentration vs. time, which gives the pseudo-first-order rate constants for reactions from the slope, revealed that pyrite had a marked effect on the rate of hydrolysis of GGG (Table 3). The other minerals tested gave results that were roughly the same as the control reaction. Notably, the pyrite reactions also had the second smallest available surface area of all of the minerals tested, underscoring the likely catalytic enhancement afforded by the surface.

As can be seen, montmorillonite appears to slightly inhibit the hydrolysis of GGG. When the rates are normalized to the amount of surface area of mineral in each reaction, calcite also appears to be highly catalytic, as does rutile.

The yields of GG and DKP vs. time for pyrite experiments are shown in Fig. 2. The initial rise and subsequent decay of the yield of DKP strongly suggests an A → B → C kinetic scheme (GGG → DKP + Gly, DKP → GG). This result suggests that the principle mechanism of hydrolysis of GGG is via the tail-biting mechanism, which produces DKP and glycine (Steinberg and Bada, 1981, 1983).

3.8. Catalytic activity of pyrite

Since pyrite appeared to be the most active surface, we set out to examine the influence of surface area and solute

Table 3
Pseudo-first-order rate constants for the hydrolysis of GGG in the presence of mineral surfaces at 70 °C and pH 8.

Mineral	Rate of hydrolysis of GGG (h^{-1})	Rate of hydrolysis of GG (h^{-1}/m^2)
Control	-3.60×10^{-3}	nd
Montmorillonite	-3.02×10^{-3}	-1.24×10^{-3}
Calcite	-3.60×10^{-3}	-9.25×10^{-2}
Silica	-3.69×10^{-3}	-7.69×10^{-5}
Rutile	-3.74×10^{-3}	-1.51×10^{-2}
Hematite	-3.80×10^{-3}	-7.61×10^{-3}
Pyrite	-5.31×10^{-3}	-9.45×10^{-2}

nd, not determined.
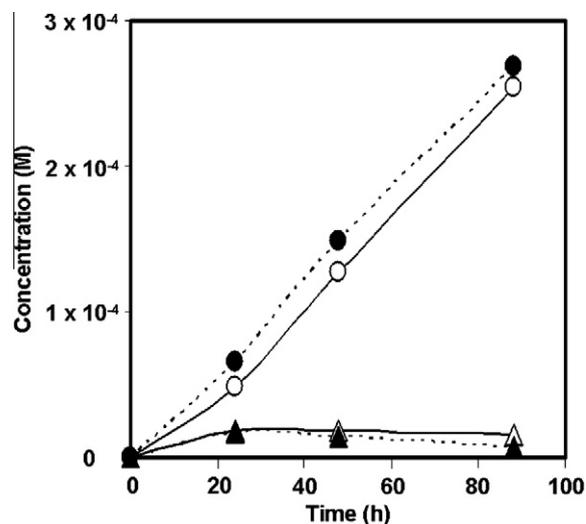
Fig. 2. Yields of GG (circles) and DKP (triangles) vs. time for the reaction of pyrite (filled symbols) or a control containing no mineral (open symbols) with GGG at pH 8 and 70 °C. The lines (dashed for pyrite reaction, solid for control) are merely intended as guides for the eye. Error bars are smaller than the symbol size.

concentration on the kinetics of GGG hydrolysis. Experiments were carried out with varying amounts of pyrite, and varying solution concentrations of GGG, or with the mineral surface area held constant and the solution concentration varied. Results are shown in Figs. 3 and 4.

Examination of the rate as a function of the amount of pyrite added shows typical conversion from first-order to zeroth-order kinetics associated with rate-limiting surface adsorption (Pilling and Saekins, 1999).

As can be seen, the rate is scarcely affected by concentration in control reactions in this concentration range, but again appears to saturate as the ratio of amino acid concentration to surface area increases, appearing to approach the background solution hydrolysis rate at infinite concentration.
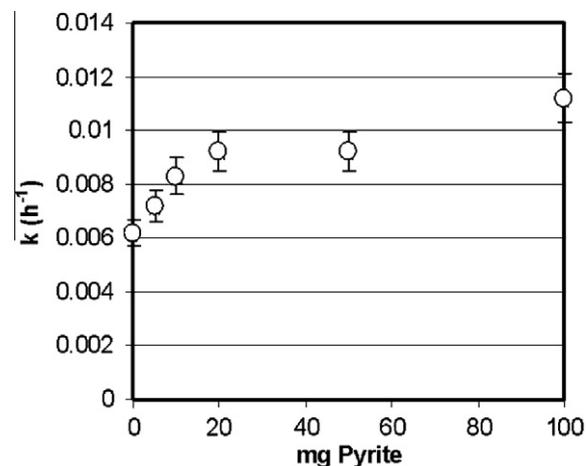
Fig. 3. Rate of hydrolysis of GGG as function of the amount of pyrite added to the reaction for initial 0.001 M GGG concentration at 70 °C at pH 8.1. Reaction volume was 1.5 mL. X-axis error bars are smaller than the symbol size.
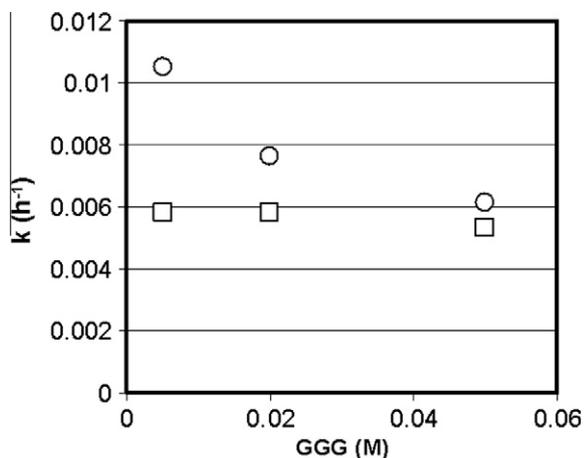
Fig. 4. Rate of hydrolysis of GGG as a function of solution concentration of GGG with a constant 10 mg amount of pyrite at pH 8.1. Reaction volume was 1.5 mL. ○, reactions in the presence of pyrite; □, control reactions with no mineral. Error bars are smaller than the symbol size.

Under our experimental regime, mineral surfaces do not appear to overcome the thermodynamically determined glycine/peptide equilibrium. Within the narrow range of pH and solute/surface area investigated there was little observable effect on the kinetics of the approach to equilibrium with respect to control reactions with the exception of pyrite, and then only in the case of GGG. The effects of mineral surfaces on the generation of higher oligomers such as G4–G6 were not extensively investigated, however, traces of Gly5 were generated from 0.01 M GGG, suggesting an initial small amount of generation of higher peptides when these peptides were added originally. This should not be interpreted to mean that the mineral surfaces can alter this equilibrium, as starting with a disequilibrium amount of a higher peptide is in itself artificial.

These conclusions might change with different amino acids or minerals, for example polyelectrolytes such as polyaspartate, polyglutamate, polyarginine or mixed polymers might be adsorbed considerably more strongly (Pradier et al., 2007).

Greenland et al. (1962, 1965) measured the free energy of adsorption as a function of chain length for glycine oligomers on montmorillonite and found the $\Delta\Delta G$ to be ~0.5 kcal/residue, while Kalra et al. (2003) found a value of ~0.2 kcal/mol, significantly less than the 3.5 kcal/mol liberated upon peptide hydrolysis (Flegmann and Tattersall, 1979; Martin, 1998). Basiuk et al. (1995) and Basiuk and Gromovoy (1996) found a similar energetic contribution per residue for the adsorption of oligoglycines on SiO_2. It can likely thus be postulated that mineral adsorption under conditions where oligomer solubility is not a factor, such as in submarine hydrothermal vents, does not alter the total adsorbed and solution-phase monomer/oligomer equilibrium significantly.

These results suggest that under aqueous conditions several common minerals catalyze the hydrolysis of some simple polypeptides, such as GGG. They may also slightly shift the total adsorbed and solution-phase equilibrium in favor of peptide elongation. Following the considerations of Lahav and Chang (1976) and De Duve and Miller (1991), there is little evidence to suggest that the incremental addition of monomers to a growing peptide chain is significantly altered by mineral adsorption. There may be some small though significant contribution to the monomer/polymer equilibrium afforded by mineral adsorption, however, it is not readily measurable in dilute solution. These results suggest that if peptides were important for the origin of life, their occurrence would have been favored in some environments such as evaporative ones. This would also have been governed by the availability of condensation reagents (Leman et al., 2004; Mita et al., 2005).

We have only investigated one type of polymer, a small fraction of the ~4400 naturally occurring mineral types (Hazen et al., 2008), a narrow temperature range (25–70 °C), and one pH value (8.1). Hydrolysis rates would likely be higher at larger pH extremes and the maximal rate of peptide elongation is likely to be near the pI of glycine and its oligomers, ~6 at 25 °C (Cleaves et al., 2009), although the stability of peptides is likely maximal at slightly higher values.

It has been reported that the reaction of pyrite surfaces with water forms hydroxyl radicals, which decompose biopolymers (Cohn et al., 2004). This could be one reason why the hydrolysis of GGG is enhanced in the presence of pyrite, however, we do see near complete conversion of the peptides into smaller peptides and amino acids via what appears to be a simple hydrolytic mechanism.

It is interesting to note that calcite preliminarily appears to be an effective catalyst for the hydrolysis of GGG. Vallentyne (1964) and Hare and Mitterer (1969) also noted that the rate of decomposition of amino acids themselves was much greater in the presence of $CaCO_3$ from *Mercenaria* shell, although Vallentyne claimed that this was likely due to some contaminants in the mineral, since pure $CaCO_3$ did not show this effect.

In dilute solution, and where the ratio of amino acid to mineral surface area is low, in the absence of activating reagents, minerals do not appear to alter the equilibrium of peptide formation, and may be true catalysts. If peptides were required for the origin of life they either (1) were produced under concentrated conditions that would suggest an evaporitic or other anhydrous (Ohara et al., 2007) environment or (2) were coupled to some sort of chemical activation such as COS (Leman et al., 2004). If this were true, it would depend on the coupling of a specific coupling reagent which would have to be extremely energetically favorable but kinetically controlled, the hallmarks of biological protein synthesis. This would seem to be a difficult set of criteria for a small molecule to fulfill. For example any activating reagent needs to be reactive with an amino acid functional group, either the amine or the carboxylic acid group (Miller and Orgel, 1974). This activated functional group would then need to be reactive with another amino acid. It does seem easier for the amino group to attack an activated carboxyl group mechanistically, indeed both biology and most laboratory peptide syntheses use this mechanism (Miller and Orgel, 1974; Liu and Orgel, 1998a). Examples of this group transfer include reagents such as cyanate (Flores and Leckie, 1973), urea (Mita et al., 2005), COS

(Leman et al., 2004), high-energy phosphates (Chung et al., 1971), CO_2 (Taillades et al., 1998), amides (Yanagawa et al., 1984) and thioesters (Maurel and Orgel, 2000; Bertrand et al., 2001).

Such reagents would also need to compete with other nucleophiles present in solution such as SH^-, NH_3 and OH^-, as well as metal ion catalyzed peptide hydrolysis (Cronin et al., 1971; Long et al., 1971; Hay and Morris, 1976). At pH 8 and 25 °C the concentration of OH^- is 10^{-6} M, which is comparable to the estimated concentration of amino acids in the primitive oceans mentioned above. (SH^-) is likely to be considerably more concentrated in hydrothermal systems (von Damm, 1995) than amino acids are. It thus seems improbable that kinetically uncontrolled non-specific activation could provide a means for producing significant amounts of oligopeptides in dilute solution, beyond the thermodynamically expected values.

There are several possible escapes from this conundrum: specific catalysis was essential for peptide elongation from very early in evolution, coupled energy transduction was essential for the evolution of peptides, or phase separation drove peptide synthesis. Organocatalysis (MacMillan, 2008) may have been important very early in the evolution of peptide synthesis, due to the much higher potential degree of three-dimensional ordering of catalytic groups compared with mineral surfaces.

Finally we note that previous experiments documenting the synthesis of peptides under drying conditions have at times shown evidence of mineral catalysis (Lahav et al., 1975; Bujdák and Rode, 1996, 1997; Plankensteiner et al., 2004), however, catalysis of cyclization and hydrolysis of GG on alumina and silica has also been noted (Bujdák and Rode, 1997). In this respect, depending on water activity and temperature, the equilibrium achieved still appears to be close to the normal thermodynamic one, yielding small amounts of dipeptides and even smaller amounts of longer oligomers. As small as these yields may be, they are considerably higher than those achieved in dilute solution, the simple explanation being that the concentrations of starting materials are higher. This underscores the likely inadequacy of aqueous environments such as marine hydrothermal systems or the open ocean for peptide synthesis. One possible, though as yet experimentally unconfirmed, escape from this concentration limitation is the concept of thermophoresis in porous minerals (Baaske et al., 2007).

Several studies have noted the catalytic effect of mineral surfaces on the hydrolysis of other types of biomolecules, for example the deamination of adenine on montmorillonite (Strašák and Šeršeň, 1991) and the hydrolysis of various sugar–phosphate esters on montmorillonite (Baldwin et al., 1995).

Mineral surfaces may have served as abiotic analogues of enzymes, carrying out primitive versions of the functions of stabilizing transition states, increasing effective concentration and presenting appropriately spatially juxtaposed catalytic sites. As such, they are at a disadvantage with respect to genetic organocatalysts in that they cannot be selected to increase their specific activity with regard to any particular reaction mechanism. The efficiency of any catalyst depends on the strength of attachment to substrates, products, and transition state intermediates, and the degree of rate enhancement (Albery and Knowles, 1976). Mineral surfaces may be catalytic for peptide bond formation, but they are also catalytic for peptide bond hydrolysis, thus thermodynamic equilibrium, concentration and the availability of chemical activating species likely ultimately determine the degree to which new chemical bonds can be formed.

4. CONCLUSIONS

The picture emerging from the accumulated evidence is that many common mineral surfaces, such as pyrite, calcite and rutile, are true catalysts for peptide bond synthesis and hydrolysis, but by themselves cannot explain the prebiotic synthesis of peptides. It seems likely that even small peptides could not have reached significant concentrations based on thermodynamic considerations without the assistance of a coupling reagent or activation process.

Amino acids are among the simplest and most abundant prebiotic compounds. Peptides appear to be the most versatile catalytic polymers nature has yet devised (Narlikar and Herschlag, 1997). What allows the coupling of these two powerful aspects of catalysis is a recursive energy transducing mechanism coupled with a heritable mechanism for reproducing these catalysts. This may seem an evasive conclusion, but it points directly towards a variety of chemical conditions that must be fulfilled for organic evolution to occur. It may be unproductive to expect any geochemical system to overcome these thermodynamic barriers without the inclusion of informational coupling and/or energy transduction.

REFERENCES

Abelson P. H. (1959) Geochemistry of organic substances. In *Researches in Geochemistry* (ed. P. H. Abelson). Wiley, New York., pp. 79–103.

Abelson P. H. (1966) Chemical events on the primitive Earth. *Proc. Natl. Acad. Sci. USA* **55**, 1365–1372.

Albery W. J. and Knowles J. R. (1976) Evolution of enzyme function and the development of catalytic efficiency. *Biochemistry* **15**, 5631–5640.

Andersson E. and Holm N. G. (2000) The stability of some selected amino acids under attempted redox constrained hydrothermal conditions. *Orig. Life Evol. Biosph.* **30**, 9–23.

Aubrey A. D., Cleaves H. J. and Bada J. L. (2009) Organic synthesis in submarine hydrothermal vent systems: I. Amino acids. *Orig. Life Evol. Biosph.* **39**, 91–108.

Baaske P., Weinert F. M., Duhr S., Lemke K. H., Russell M. J. and Braun D. (2007) Extreme accumulation of nucleotides in simulated hydrothermal pore systems. *Proc. Natl. Acad. Sci. USA* **104**, 9346–9351.

Bada J. L., Miller S. L. and Zhao M. (1995) The stability of amino acids at submarine hydrothermal vent temperatures. *Orig. Life Evol. Biosph.* **25**, 111–118.

Baldwin D. S., Beattie J. K., Coleman L. M. and Jones D. R. (1995) Phosphate ester hydrolysis facilitated by mineral phases. *Environ. Sci. Technol.* **29**, 1706–1709.

Basiuk V. A. and Gromovoy T. U. (1996) Comparative study of amino acid adsorption on bare and octadecyl silica from water using high-performance liquid chromatography. *Colloids Surf. A* **118**, 127–140.

Basiuk V. A., Gromovoy T. U. and Khil'Chevskaya E. G. (1995) Adsorption of small biological molecules on silica from diluted aqueous solutions: quantitative characterization and implications to the Bernal's hypothesis. *Orig. Life Evol. Biosph.* **25**, 375–393.

Bernal J. D. (1951) *The Physical Basis of Life*. Routledge, London.

Bertrand M., Bure C., Fleury F. and Brack A. (2001) Prebiotic polymerisation of amino acid thioesters on mineral surfaces. In *Geochemistry and the Origin of Life* (eds. S. Nakashima, S. Maruyama, A. Brack and B. F. Windley). Universal Academy Press, Tokyo, pp. 51–60.

Bujdák J. and Rode B. (1996) Clays and catalysis of prebiotic peptide bond formation. *Acta Univ. Carol. Geol.* **38**, 139–143.

Bujdák J. and Rode B. M. (1997) Glycine oligomerization on silica and alumina. *React. Kinet. Catal. Lett.* **62**, 281–286.

Chang S. (1988) Planetary environments and the conditions of life. *Philos. Trans. R. Soc. Lond. A* **325**, 601–610.

Chang S., Flores J. and Ponnamperuma C. (1969) Peptide formation mediated by hydrogen cyanide tetramer: a possible prebiotic process. *Proc. Natl. Acad. Sci. USA* **64**, 1011–1015.

Chung N. M., Lohrmann R., Orgel L. E. and Rabinowitz J. (1971) The mechanism of the trimetaphosphate-induced peptide synthesis. *Tetrahedron* **27**, 1205–1210.

Churchill H., Teng H. and Hazen R. M. (2004) Correlation of pH-dependent surface interaction forces to amino acid adsorption: implications for the origin of life. *Am. Mineral.* **89**, 1048–1055.

Chyba C. and Sagan C. (1992) Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* **355**, 125–132.

Cleaves H. J. and Lazcano A. (2009) Origin of biomolecules. In *Chemical Evolution: II. From Origins of Life to Modern Society* (eds. L. Zaikowski and J. M. Friedrich). Oxford University Press, New York.

Cleaves H. J., Aubrey A. D. and Bada J. L. (2009) An evaluation of the critical parameters for abiotic peptide synthesis in submarine hydrothermal systems. *Orig. Life Evol. Biosph.* **39**, 109–126.

Cohn C. A., Borda M. J. and Schoonen M. A. (2004) RNA decomposition by pyrite-induced radicals and possible role of lipids during the emergence of life. *Earth Planet. Sci. Lett.* **225**, 271–278.

Cronin J. R., Long D. A. and Truscott T. G. (1971) Peptide kinetics: Part 12. The effect of Zn (II) on the reaction of some glycine-containing dipeptides and diketopiperazines at pH 5.6 and 368.2 K. *Trans. Faraday Soc.* **67**, 2096–2100.

Dashman T. and Stotzky G. (1984) Adsorption and binding of peptides on homoionic montmorillonite and kaolinite. *Soil Biol. Biochem.* **16**, 51–55.

de Duve C. (2003) A research proposal on the origin of life. *Orig. Life Evol. Biosph.* **33**, 559–574.

de Duve C. and Miller S. L. (1991) Two-dimensional life? *Proc. Natl. Acad. Sci. USA* **88**, 10014–10017.

Dobry A., Fruton J. S. and Sturtevant J. M. (1952) Thermodynamics of hydrolysis of peptide bonds. *J. Biol. Chem.* **195**, 149–154.

Dose K. (1983) Prebiotic polypeptides and the origin of biological information. *Naturwissenschaften* **70**, 378–382.

Elsila J. E., Glavin D. P. and Dworkin J. P. (2009) Cometary glycine detected in samples returned by Stardust. *Meteorit. Planet. Sci.* **44**, 1323–1330.

Faisal M., Daimon H. and Fujie K. (2008) Hydrolysis of glycylglycine in subcritical water conditions. *J. Phys. Conf. Ser.* **121**, 1–6.

Flegmann A. W. and Scholefield D. (1978) Thermodynamics of peptide bond formation at clay mineral surfaces. *J. Mol. Evol.* **12**, 101–112.

Flegmann A. W. and Tattersall R. (1979) Energetics of peptide bond formation at elevated temperatures. *J. Mol. Evol.* **12**, 349–355.

Flores J. J. and Leckie J. O. (1973) Peptide formation mediated by cyanate. *Nature* **244**, 435–437.

Fox S. W. and Harada K. (1958) Thermal copolymerization of amino acids to a product resembling protein. *Science* **128**, 1214.

Greenland D. J., Laby R. H. and Quirk J. P. (1962) Adsorption of glycine and its di-, tri-, and tetra-peptides by montmorillonite. *Trans. Faraday Soc.* **58**, 829–841.

Greenland D. J., Laby R. H. and Quirk J. P. (1965) Adsorption of amino-acids and peptides by montmorillonite and illite: Part 2. Physical adsorption. *Trans. Faraday Soc.* **61**, 2024–2035.

Grotzinger J. P. and Kasting J. F. (1993) New constraints on Precambrian ocean composition. *J. Geol.* **101**, 235–243.

Hare P. E. and Mitterer R. M. (1969) Laboratory simulation of amino acid diagenesis in fossils. *Carnegie Inst. Wash. Yearb.* **67**, 205–210.

Hawker, Jr., J. R. and Oró J. (1981) Cyanamide mediated syntheses of peptides containing histidine and hydrophobic amino acids. *J. Mol. Evol.* **17**, 285–294.

Hay R. W. and Morris P. J. (1976) Metal ion-promoted hydrolysis of amino acid esters and peptides. *Met. Ions Biol. Syst.* **5**, 173–243.

Hazen R. M. and Sverjensky D. A. (2010) Mineral surfaces, geochemical complexities, and the origins of life. In *Additional Perspectives on the Origin of Life*. Cold Spring Harbor Perspectives in Biology (eds. D. D. Deamer and J. W. Szostak). doi:10.1101/cshperspect.a002162.

Hazen R. M., Papineau D., Bleeker W., Downs R. T., Ferry J. M., McCoy T. J., Sverjensky D. A. and Yang H. X. (2008) Mineral evolution. *Am. Mineral.* **93**, 1693–1720.

Hill, Jr., A. R., Böhler C. and Orgel L. E. (1998) Polymerization on the rocks: negatively-charged α-amino acids. *Orig. Life Evol. Biosph.* **28**, 235–243.

Ikehara K. (2009) Pseudo-replication of [GADV]-proteins and origin of life. *Int. J. Mol. Sci.* **10**, 1525–1537.

Imai E., Honda H., Hatori K., Brack A. and Matsuno K. (1999) Elongation of oligopeptides in a simulated submarine hydrothermal system. *Science* **283**, 831–833.

Johnson A. P., Cleaves H. J., Dworkin J. P., Glavin D. P., Lazcano A. and Bada J. L. (2008) The Miller volcanic spark discharge experiment. *Science* **322**, 404.

Jonsson C. M., Jonsson C. L., Sverjensky D. A., Cleaves H. J. and Hazen R. M. (2009) Attachment of L-glutamate to rutile (α-TiO$_2$): a potentiometric, adsorption, and surface complexation study. *Langmuir* **25**, 12127–12135.

Jonsson C. M., Jonsson C. L., Estrada C., Sverjensky D. A., Cleaves H. J. and Hazen R. M. (2010) Adsorption of L-aspartate to rutile (α-TiO$_2$): experimental and theoretical surface complexation studies. *Geochim. Cosmochim. Acta* **74**, 2356–2367.

Kahne D. and Still W. C. (1988) Hydrolysis of a peptide bond in neutral water. *J. Am. Chem. Soc.* **110**, 7529–7534.

Kalra S., Pant C. K., Pathak H. D. and Mehata M. S. (2003) Studies on the adsorption of peptides of glycine/alanine on montmorillonite clay with or without co-ordinated divalent cations. *Colloids Surf. A* **212**, 43–50.

Kauffman S. A. (1971) Cellular homeostasis, epigenesis and replication in randomly aggregated macromolecular systems. *Cybern. Syst.: Int. J.* **1**, 71–96.

Kelley D. S., Karson J. A., Früh-Green G. L., Yoerger D. R., Shank T. M., Butterfield D. A., Hayes J. M., Schrenk M. O., Olson E. J., Proskurowski G., Jakuba M., Bradley A., Larson B., Ludwig K., Glickson D., Buckman K., Bradley A. S., Brazelton W. J., Roe K., Elend M. J., Delacour A., Bernasconi S. M., Lilley M. D., Baross J. A., Summons R. E. and Sylva S. P. (2005) A serpentinite-hosted ecosystem: the Lost City hydrothermal field. *Science* **307**, 1428–1434.

Kempe S. and Kazmierczak J. (2002) Biogenesis and early life on Earth and Europa: favored by an alkaline ocean? *Astrobiology* **2**, 123–130.

Knauth L. P. and Lowe D. R. (2003) High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland Supergroup, South Africa. *Geol. Soc. Am. Bull.* **115**, 566–580.

Kozai T., Hayashi N. and Ikeda Y. (1975) Ring-opening polymerization of piperazine-2,5-dione in the presence of aqueous ammonia. *Kobunshi Ronbunshu Eng. Ed.* **4**, 64–70.

Kvenvolden K., Lawless J., Pering K., Peterson E., Flores J., Ponnamperuma C., Kaplan I. R. and Moore C. (1970) Evidence for extraterrestrial amino-acids and hydrocarbons in the Murchison meteorite. *Nature* **228**, 923–926.

Lahav N. and Chang S. (1976) The possible role of solid surface area in condensation reactions during chemical evolution: reevaluation. *J. Mol. Evol.* **8**, 357–380.

Lahav N., White D. and Chang S. (1975) Peptide formation in the prebiotic era: thermal condensation of glycine in fluctuating clay environments. *Science* **201**, 67–69.

Lambert J. (2008) Adsorption and polymerization of amino acids on mineral surfaces: a review. *Orig. Life Evol. Biosph.* **38**, 211–242.

Leman L., Orgel L. and Ghadiri M. R. (2004) Carbonyl sulfide-mediated prebiotic formation of peptides. *Science* **306**, 283–286.

Li J. and Brill T. B. (2003a) Spectroscopy of hydrothermal reactions: Part 26. Kinetics of decarboxylation of aliphatic amino acids and comparison with the rates of racemization. *Int. J. Chem. Kinet.* **35**, 602–610.

Li J. and Brill T. B. (2003b) Spectroscopy of hydrothermal reactions: 25. Kinetics of the decarboxylation of protein amino acids and the effect of side chains on hydrothermal stability. *J. Phys. Chem. A* **107**, 5987–5992.

Li J. and Brill T. B. (2003c) Spectroscopy of hydrothermal reactions: 27. Simultaneous determination of hydrolysis rate constants of glycylglycine to glycine and glycylglycine–diketopiperazine equilibrium constants at 310–330 °C and 275 bar. *J. Phys. Chem. A* **107**, 8575–8577.

Liu R. and Orgel L. E. (1998a) Polymerization of amino acids in aqueous solution. *Orig. Life Evol. Biosph.* **28**, 47–60.

Liu R. and Orgel L. E. (1998b) Polymerization on the rocks: β-amino acids and arginine. *Orig. Life Evol. Biosph.* **28**, 245–257.

Long D. A., Truscott T. G., Cronin J. R. and Lee R. G. (1971) Peptide kinetics: Part 11. Influence of divalent metal ions on rate of reaction of glycyl-glycine in the pH ranges 0.3–1.0 and 3.8–6.0. *Trans. Faraday Soc.* **67**, 1094–1103.

Lowe C. U., Rees M. W. and Markham R. (1963) Synthesis of complex organic compounds from simple precursors: formation of amino-acids, amino-acid polymers, fatty acids and purines from ammonium cyanide. *Nature* **199**, 219–222.

MacMillan D. W. C. (2008) The advent and development of organocatalysis. *Nature* **455**, 304–308.

Marshall W. L. (1994) Hydrothermal synthesis of amino acids. *Geochim. Cosmochim. Acta* **58**, 2099–2106.

Martin R. B. (1998) Free energies and equilibria of peptide bond hydrolysis and formation. *Biopolymers* **45**, 351–353.

Maurel M. and Orgel L. E. (2000) Oligomerization of α-thioglutamic acid. *Orig. Life Evol. Biosph.* **30**, 423–430.

Meggy A. B. (1953) Glycine peptides: I. The polymerization of 2,5-piperazinedione at 180°. *J. Chem. Soc.*, 851–855.

Meggy A. B. (1956) Glycine peptides: II. Heat and entropy of formation of the peptide bond in polyglycine. *J. Chem. Soc.*, 1444–1454.

Miller S. L. (1953) A production of amino acids under possible primitive earth conditions. *Science* **117**, 528–529.

Miller S. L. (1955) Production of some organic compounds under possible primitive Earth conditions. *J. Am. Chem. Soc.* **77**, 2351–2361.

Miller S. L. and Orgel L. E. (1974) *The Origins of Life on the Earth*. Prentice Hall, Englewood Cliffs, NJ.

Mita H., Nomoto S., Terasaki M., Shimoyama A. and Yamamoto Y. (2005) Prebiotic formation of polyamino acids in molten urea. *Int. J. Astrobiol.* **4**, 145–154.

Morse J. W. and Mackenzie F. T. (1998) Hadean ocean carbonate geochemistry. *Aquat. Geochem.* **4**, 301–319.

Nagayama M., Takaoka O., Inomata K. and Yamagata Y. (1990) Diketopiperazine-mediated peptide formation in aqueous solution. *Orig. Life Evol. Biosph.* **20**, 249–257.

Narlikar G. J. and Herschlag D. (1997) Mechanistic aspects of enzymatic catalysis: lessons from comparison of RNA and protein enzymes. *Annu. Rev. Biochem.* **66**, 19–59.

Ohara S., Kakegawa T. and Nakazawa H. (2007) Pressure effects on the abiotic polymerization of glycine. *Orig. Life Evol. Biosph.* **37**, 215–223.

Orgel L. E. (1998) Polymerization on the rocks: theoretical introduction. *Orig. Life Evol. Biosph.* **28**, 227–234.

Oró J. and Kamat S. (1961) Amino-acid synthesis from hydrogen cyanide under possible primitive Earth conditions. *Nature* **190**, 442–443.

Parks G. A. (1965) The isoelectric points of solid oxides, solid hydroxides, and aqueous hydroxo complex systems. *Chem. Rev.* **65**, 177–198.

Pilling M. J. and Saekins P. W. (1999) *Reaction Kinetics*. Oxford University Press, Oxford, UK.

Plankensteiner K., Reiner H. and Rode B. M. (2004) From Earth's primitive atmosphere to chiral peptides – the origin of precursors for life. *Chem. Biodivers.* **1**, 1308–1315.

Ponnamperuma C., Shimoyama A. and Friebele E. (1982) Clays and the origin of life. *Orig. Life* **12**, 9–40.

Porter T. L., Eastman M. P., Hagerman M. E., Price L. B. and Shand R. F. (1998) Site-specific prebiotic oligomerization reactions of glycine on the surface of hectorite. *J. Mol. Evol.* **47**, 373–377.

Pradier C. M., Humblot V., Stievano L., Méthivier C. and Lambert J. F. (2007) Salt concentration and pH-dependent adsorption of two polypeptides on planar and divided alumina surfaces. In situ IR investigations. *Langmuir* **23**, 2463–2471.

Qian Y., Engel M. H., Macko S. A., Carpenter S. and Deming J. W. (1993) Kinetics of peptide hydrolysis and amino acid decomposition at high temperature. *Geochim. Cosmochim. Acta* **50**, 813–823.

Radzicka A. and Wolfenden R. (1996) Rates of uncatalyzed peptide bond hydrolysis in neutral solution and the transition state affinities of proteases. *J. Am. Chem. Soc.* **118**, 6105–6109.

Rode B. M., Son H. L., Suwannachot Y. and Bujdak J. (1999) The combination of salt induced peptide formation reaction and

clay catalysis: a way to higher peptides under primitive earth conditions. *Orig. Life Evol. Biosph.* **29**, 273–286.

Russell M. J. and Hall A. J. (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. *J. Geol. Soc. (London)* **154**, 377–402.

Schoonen M., Smirnov A. and Cohn C. (2004) A perspective on the role of minerals in prebiotic synthesis. *Ambio* **33**, 539–551.

Schwartz A. W. (1981) Chemical evolution – the genesis of the first organic compounds. In *Marine Organic Chemistry* (eds. E. K. Duursma and R. Dawson). Elsevier Oceanography Series, Amsterdam, pp. 7–30.

Sillén L. G. (1967) The ocean as a chemical system. *Science* **156**, 1189–1197.

Snider M. J. and Wolfenden R. (2000) The rate of spontaneous decarboxylation of amino acids. *J. Am. Chem. Soc.* **122**, 11507–11508.

Steinberg S. and Bada J. L. (1981) Diketopiperazine formation during investigations of amino acid racemization in dipeptides. *Science* **213**, 544–545.

Steinberg S. and Bada J. L. (1983) Peptide decomposition in the neutral pH region via the formation of diketopiperazines. *J. Org. Chem.* **48**, 2295–2298.

Strašák M. and Seršeň F. (1991) An unusual reaction of adenine and adenosine on montmorillonite. *Naturwissenschaften* **78**, 121–122.

Stribling R. and Miller S. L. (1987) Energy yields for hydrogen cyanide and formaldehyde syntheses: the HCN and amino acid concentrations in the primitive ocean. *Orig. Life Evol. Biosph.* **17**, 261–273.

Sverjensky D. A., Jonsson C. M., Jonsson C. L., Cleaves H. J. and Hazen R. M. (2008) Glutamate surface speciation on amorphous titanium dioxide and hydrous ferric oxide. *Environ. Sci. Technol.* **42**, 6034–6039.

Taillades J., Beuzelin I., Garrel L., Tabacik V., Bied C. and Commeyras A. (1998) N-carbamoyl-alpha-amino acids rather than free-alpha-amino acids formation in the primitive hydrosphere: a novel proposal for the emergence of prebiotic peptides. *Orig. Life Evol. Biosph.* **28**, 61–77.

Vallentyne J. R. (1964) Biogeochemistry of organic matter: II. Thermal reaction kinetics and transformation products of amino acids. *Geochim. Cosmochim. Acta* **28**, 157–188.

Von Damm K. L. (1995) Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In *Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions* (eds. S. E. Humphris, R. A. Zierenberg, L. S. Mullineaux and R. E. Thomson). AGU, Washington, DC, pp. 222–247.

Wächtershäuser G. (1988) Before enzymes and templates: theory of surface metabolism. *Microbiol. Rev.* **52**, 452–484.

Weerasooriy R. and Tobschall H. J. (2005) Pyrite–water interactions: effects of pH and pFe on surface charge. *Colloids Surf. A* **264**, 68–74.

White R. H. (1984) Hydrolytic stability of biomolecules at high temperatures and its implication for life at 250 °C. *Nature* **310**, 430–432.

Yanagawa H., Nishizawa M. and Kojima K. (1984) A possible prebiotic peptide formation from glycinamide and related compounds. *Orig. Life* **14**, 267–272.

Zaia D. A. M. (2004) A review of adsorption of amino acids on minerals: was it important for origin of life? *Amino Acids* **27**, 113–118.

Zhou Q., Maurice P. A. and Cabaniss S. E. (2001) Size fractionation upon adsorption of fulvic acid on goethite: equilibrium and kinetic studies. *Geochim. Cosmochim. Acta* **65**, 803–812.

Associate editor: Kevin M. Rosso