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Role of manganese oxides in peptide synthesis: implication in chemical evolution

Brij Bhushan[1], Arunima Nayak[2] and Kamaluddin[3]

[1]*Department of Agrifood Engineering and Biotecnology, Universitat Politècnica de Catalunya (UPC), Castelldefels, Barcelona 08860, Spain e-mail: brijbhushaniitr@gmail.com*
[2]*IRIS Research-Engineering-Technology, Castelldefels, Barcelona 08860, Spain*
[3]*Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667 (Uttrakhand), India*

Abstract: During the course of chemical evolution the role of metal oxides may have been very significant in catalysing the polymerization of biomonomers. The peptide bond formation of alanine (ala) and glycine (gly) in the presence of various oxides of manganese were performed for a period of 35 days at three different temperatures 50, 90 and 120°C without applying drying/wetting cycling. The reaction was monitored every week. The products formed were characterized by high-performance liquid chromatography and electrospray ionization–mass spectrometry techniques. Trace amount of oligomers was observed at 50°C. Maximum yield of peptides was found after 35 days at 90°C. It is important to note that very high temperatures of 120°C favoured the formation of diketopiperazine derivatives. Different types of manganese oxides [manganosite (MnO), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4) and pyrolusite (MnO_2)] were used as catalyst. The MnO catalysed glycine to cyclic $(Gly)_2$, $(Gly)_2$ and $(Gly)_3$, and alanine, to cyclic $(Ala)_2$ and $(Ala)_2$. Mn_3O_4 also produced the same products but in lesser yield, while Mn_2O_3 and MnO_2 produced cyclic anhydride of glycine and alanine with a trace amount of dimers and trimmers. Manganese of lower oxidation state is much more efficient in propagating the reaction than higher oxidation states. The possible mechanism of these reactions and the relevance of the results for the prebiotic chemistry are discussed.

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Key words: alanine, catalysis, glycine, prebiotic peptide formation.

Introduction

The interaction of a wide variety of organic molecules such as amino acids, peptides, nucleic acid bases, nucleotides, among each other on the clay and clay minerals have been investigated in detail (Greenland *et al.* 1962, 1965a, b; Graf & Laganly 1980). These simple precursors produced eventually more complicated biopolymers (Getz 1990; Rode 1999; Voigt *et al.* 2000). The first biopolymers might have been condensed phases of peptides on the surface of minerals or other substances (Kunin 2000). Peptide-like polymers seem to be among the first macromolecules, which might have played a key role in chemical processes leading to the emergence of the first living cell (Brack & Barbier 1990). Studies have been conducted on the synthesis of peptides under hydrothermal conditions resulting in low yields of oligomeric products (Shock 1992; Amend & Shock 2000; Cleaves *et al.* 2009; Lemke *et al.* 2009) Extensive studies have documented the role of clays, minerals and inorganic oxides widely prevalent on the primitive earth in catalysing the condensation reactions of amino acids for peptide synthesis (Flegmann & Scholefield 1978; Lahav *et al.* 1978; Coyne 1985; Basiuk *et al.* 1991; Lahav 1994; Bujdak & Rode 1996, 1997a, b, 1999a, b; Zamaraev *et al.* 1997; Porter *et al.* 1998; Smith 1998; Rode *et al.* 1999; Rimola *et al.* 2006, 2007; Marshall-Bowman *et al.* 2010; Schreiner *et al.* 2011; Fuchida *et al.* 2014). The works reported in such studies have involved clay minerals, silica, alumina and other related compounds and minerals. The results strongly support the heterogeneous condensation hypothesis, which states the importance of mineral surface in aiding polymerization from biomonomers.

Like natural minerals, transition metal oxides are important constituents of the Earth crust and may have been important as catalysts for the formation of biopolymers during chemical evolution and the origin of life (Arora & Kamaluddin 2007, 2009; Arora *et al.* 2007). Recently, various studies have shown the good efficiency of transition metals and their oxides as catalysts such as hematite (Arora *et al.* 2007), zinc oxide (Arora & Kamaluddin 2007), aluminium oxide (Arora & Kamaluddin 2009), iron oxides (goethite, akaganeite and hematite) (Shanker *et al.* 2011, 2013) in the formation of several nucleobases from formamide and hence suggested their role in the prebiotic synthesis. Synthetic ferrihydrite was found to adsorb and bind amino acid and further promoted the peptide bond formation (Matrajit & Blanot 2004).

In this context, it is worth mentioning the relative abundance of manganese oxides on primitive earth (Turekian & Wedepohl 1961; Heiserman 1992) and its possible involvement in chemical evolution of life on earth. Our earlier studies have demonstrated the role of manganese oxides as a catalyst in several reactions pathways that may have led to the emergence of life (Bhushan *et al.* 2011, 2016a, b). In an effort for gaining knowledge on possible peptide bond formation, studies were undertaken on different manganese oxides [manganosite

(MnO), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4) and pyrolusite (MnO_2)] for carrying out condensation reaction for possible peptide synthesis from two model amino acids (glycine and alanine). Peptide synthesis on early Earth might have occurred at higher temperature in hydrothermal vent-like conditions (Shock 1992; Huber & Wächtershäuser 1998; Imai *et al.* 1999; Amend & Shock 2000; Huber *et al.* 2003; Cleaves *et al.* 2009; Lemke *et al.* 2009). This hypothesis was demonstrated by various works on the successful peptide synthesis occurring on mineral surfaces at higher temperatures of 80–85°C (Bujdak & Rode 1997b, 1999a, b, 2001, 2002). In the present study, attempt was made to find more diverse conditions for possible peptide formation on the various oxides of manganese surface and hence experiments were conducted in the temperature interval of 50–120°C.

Experimental procedure

Material and methods

Manganese acetate and ammonium oxalate were purchased from Merck. Alanine, glycine, sodium hexane sulphonate acidified and phosphoric acid were purchased from Sigma. All other chemicals used were of an analytical grade and were used without further purification. Millipore water was used throughout the studies.

Synthesis and characterization of the manganese oxides

Manganese oxides of different Mn/O ratio (MnO, Mn_3O_4, Mn_2O_3 and MnO_2) were synthesized as described in our earlier works (Bhushan *et al.* 2011). Characterization studies with respect to X-ray diffraction (XRD) revealed the purity of the prepared oxides after comparison with JCPDS XRD patters. The surface area of the oxides were determined by nitrogen (N) adsorption isotherms on micromeritics ASAP 2010 (UK). All manganese oxides had a more or less equal surface area. Details are described in (Bhushan *et al.* 2011).

Oligomerization of glycine and L-alanine

Each of the manganese oxides, MnO, Mn_2O_3, Mn_3O_4 and MnO_2 (0.1 g) were impregnated with aqueous solution of amino acids: glycine and L-alanine (0.1 ml, 0.1 M) separately. Each of the suspensions was dried under ambient conditions by heating for 3 h. This was initiated to undertake adsorption of the amino acids on the manganese oxide surface. The dried samples were subsequently exposed to further heating at three different temperatures of 50, 90 and 120°C for a period of 35–42 days. The reaction products formed was monitored for formation of peptide bonds after every 7 days. No fluctuating drying/wetting conditions were simulated. After every 7 days, the condensation products obtained were washed with 1 ml of 0.1 M calcium chloride solution to leach out the adsorbed amino acids and related reaction products. Control experiments of amino acids without catalyst were also performed. The supernatant liquid of the reaction was filtered and divided into two parts; one part of the filtrate was used for high-performance liquid chromatography (HPLC) analysis

Table 1. *Yield of the products formed by heating glycine and alanine in the presence of manganese oxides*

	% yield[b] of the products[c] formed when glycine and alanine were heated at 50, 90 and 120°C for 35 days											
	Cyc(Gly)$_2$			(Gly)$_2$			(Gly)$_3$			Cyc(Ala)$_2$			(Ala)$_2$		
Catalyst[a]	50°C	90°C	120°C	50°C	90°C	120°C	50°C	90°C	120°C	50°C	90°C	120°C	50°C	90°C	120°C
No catalyst	Trace	Trace	0.10 ± 0.04	Trace	Trace	Trace	–	–	–	–	–	–	–	–	–
MnO	3.4 ± 0.78	26.4 ± 1.28	28.2 ± 1.01	Trace	26.8 ± 1.29	12.8 ± 1.77	4.6 ± 0.07	16.7 ± 0.97	12.1 ± 1.05	3.9 ± 0.03	24.6 ± 1.55	36.7 ± 2.11	4.2 ± 0.57	20.2 ± 1.44	12.5 ± 1.11
Mn_3O_4	2.6 ± 0.05	20.6 ± 0.92	21.2 ± 0.73	Trace	22.8 ± 1.05	10.6 ± 0.78	Trace	12.4 ± 0.62	8.4 ± 0.66	Trace	22.3 ± 2.04	24.8 ± 1.88	2.6 ± 0.06	22.6 ± 1.32	10.4 ± 0.65
Mn_2O_3	Trace	20.8 ± 0.73	13.3 ± 1.08	Trace	21.4 ± 0.67	5.3 ± 0.52	Trace	9.5 ± 0.81	5.7 ± 0.05	Trace	12.9 ± 1.43	12.6 ± 1.00	Trace	10.2 ± 1.22	Trace
MnO_2	Trace	10.1 ± 0.41	11.0 ± 0.63	Trace	9.5 ± 0.42	Trace	Trace	7.4 ± 0.55	Trace	Trace	6.4 ± 0.67	8.5 ± 0.43	Trace	10.8 ± 1.05	Trace

[a]Reactions were performed in the presence of 100 mg of manganese oxide.
[b]Quantitative evaluation was performed by HPLC (Waters 2489, binary system) equipped with a column of Waters (Spherisorp 5 µm ODS2 4.6 mm × 250 mm). UV detection was performed at 200 nm wavelength. The mobile phase compositions were 10 mM sodium hexane sulphonate acidified with phosphoric acid to pH ~ 2.5 (solvent A) and acetonitrile of HPLC grade (solvent B), with a flow rate of 1 ml min^{-1}. The yields of products were calculated by comparing peak area with the standards.
[c]Products were identified by co- injection analysis with authentic samples.

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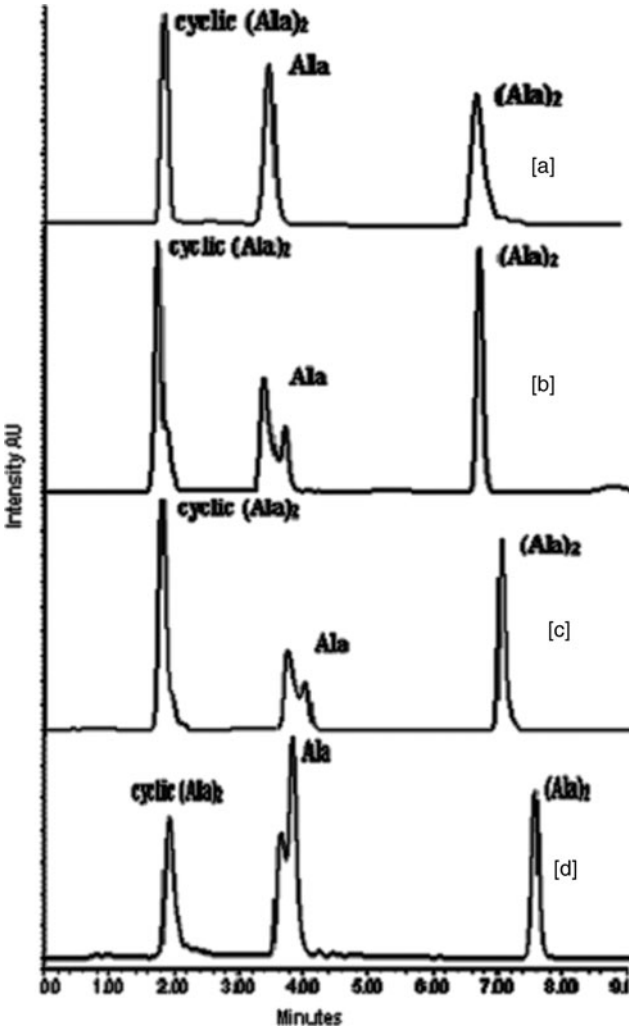

Fig. 1. HPLC chromatogram of products formed when alanine was heated at 90°C for 35 days in the presence of (a) MnO, (b) Mn_3O_4, (c) Mn_2O_3 and (d) MnO_2.

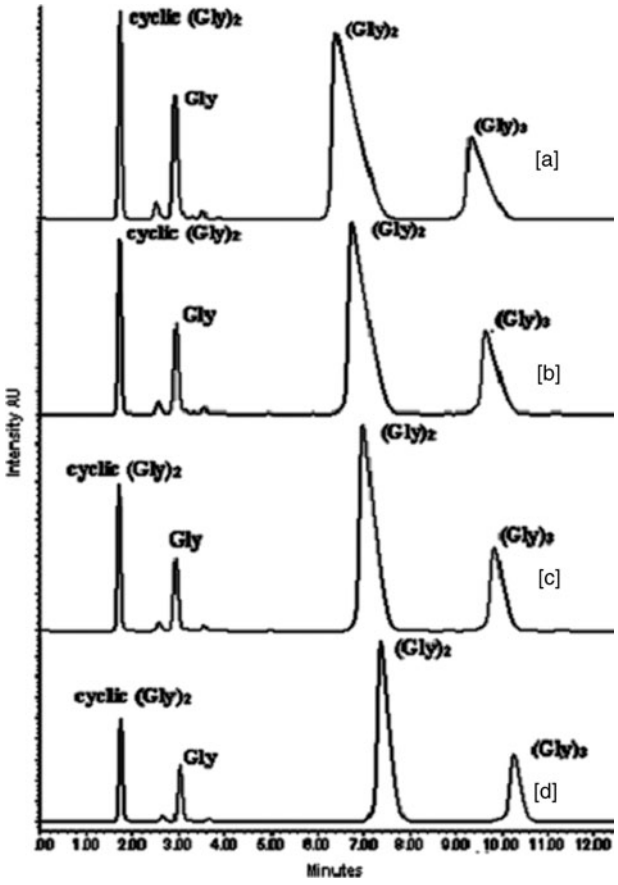

Fig. 2. HPLC chromatogram of products formed when glycine was heated at 90°C for 35 days in the presence of (a) MnO, (b)] Mo_3O_4, (c) Mn_2O_3 and (d) pyrolusite (MnO_2).

while other for electrospray ionization–mass spectrometry (ESI–MS) analysis.

HPLC analysis

All the solutions obtained from the reaction system were analysed with HPLC (Waters 2489, binary system) equipped with a column of Waters (Spherisorp 5 µm ODS2 4.6 mm × 250 mm). UV detection was performed at 200 nm wavelength. The mobile phase compositions were 10 mM sodium hexane sulphonate acidified with phosphoric acid to pH ∼ 2.5 (solvent A) and acetonitrile of HPLC grade (solvent B) with a flow rate of 1 ml min^{-1}. The reaction products were identified by retention time and co-injection method.

ESI–MS analysis

A Bruker Esquire 4000 (Bruker Daltonics Data Analysis 3.3, Germany) ion trap mass spectrometer interfaced to ESI source was used for mass analysis for the formation of peptides in the presence of manganese oxides. Ionization of analytes was carried out using the following setting of ESI: nebulizer gas flow 10 psi, dry gas 5 l min^{-1}, dry temperature 300°C, capillary voltage 4000 V. Calibration of *m*/*z* was performed using ES-tuning mix. The ESI–MS/MS experiments of the products were also performed under the same conditions using positive ionization mode.

Results

In the control experiments with glycine only, formation of a trace of Cyc(Gly)$_2$ [diketopiperazine (DKP)] and (Gly)$_2$ was observed after 35 days; however, formation of a peptide in the blank experiment of alanine was not observed, in accordance with the previous observations (Bujdak & Rode 1999a, b). The maximum yield of products was attained after 35 days, after which the yields subsequently decreased. Thus, the yield of the products obtained by heating alanine and glycine in the presence of different manganese oxides at temperatures 50, 90 and 120°C for 35 days are tabulated and shown in Table 1. Since the experiments were conducted in triplicate, Table 1 shows the standard deviation along with the average yields of the products. Representative HPLC chromatograms are shown in Figs. 1 and 2. The ESI–MS spectra of glycine, alanine and the oligomer products formed after 35 days at 90°C in the

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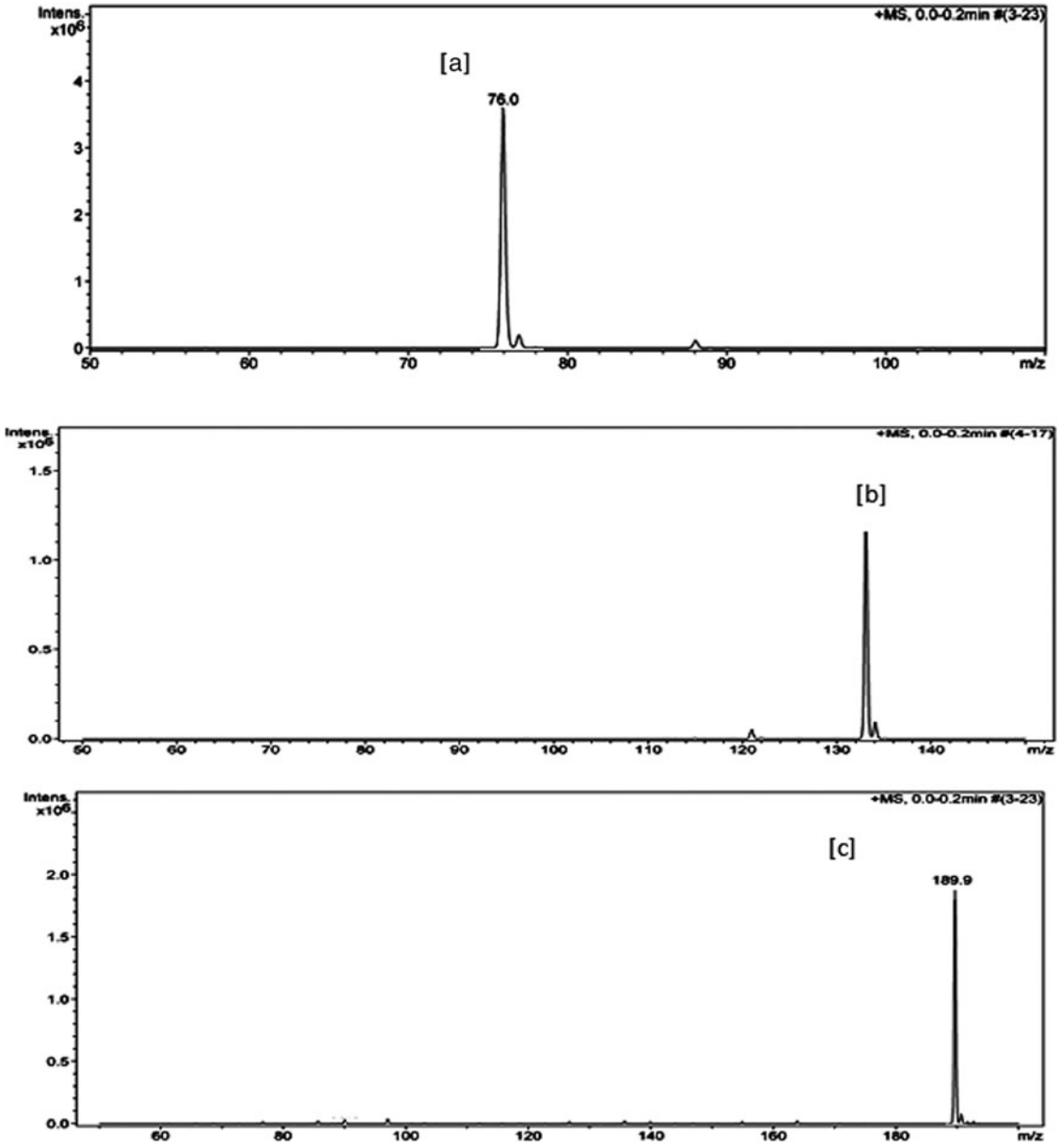

Fig. 3. ES1–MS spectra of (a) glycine, (b) glycylglycine and (c) glycylglycylglycine.

presence of MnO are depicted in Figs. 3–5, respectively. In the MS spectra of glycine, mass 76.1 corresponds to $[Gly + H]^+$, 115 for $[CycGly_2 + H]^+$, 132.9 for $[Gly_2 + H]^+$ and 189.9 for $[Gly_3 + H]^+$. In the MS spectra of alanine, mass 90.1 corresponds to $[Ala + H]^+$, 115 for $[CycAla_2 + H]^+$ and 160.9 for $[Ala_2 + H]^+$.

The reaction products were identified by retention times and co-injection method. Yields of the products were determined by comparing the peak area of products to the standards.

Discussion

The significant presence of peptides in the test experiments in comparison with those in the control, in the present study, reveals the role of manganese oxides as catalyst in the formation of polymerized products. The catalytic activity of manganese oxide is well established in the literature (Radhakrishnan & Oyama 2001; Espinal *et al.* 2004). It is used in a wide range of industrial catalytic applications, such as photocatalytic oxidation of organic pollutants, nitric oxide reduction, selective oxidations of carbon monoxide, cyclohexane, ethylbenzene, ethanol and 2-propanol, decomposition of hydrogen peroxide, hydrogenolysis of cyclopropane and oligomerization of methane. The catalytic activity of MnO for the oligomerization of amino acid can be explained on the basis of the surface active sites (Chen *et al.* 1997; Kijlstra *et al.* 1997; Zhou *et al.* 1998; Vileno *et al.* 1999; Xia *et al.* 1999; Chen *et al.* 2001; Qi & Yang 2003). The catalytic activity of manganese oxides in the activities leading to chemical evolution have been demonstrated in earlier works (Bhushan *et al.* 2011, 2016a, b).

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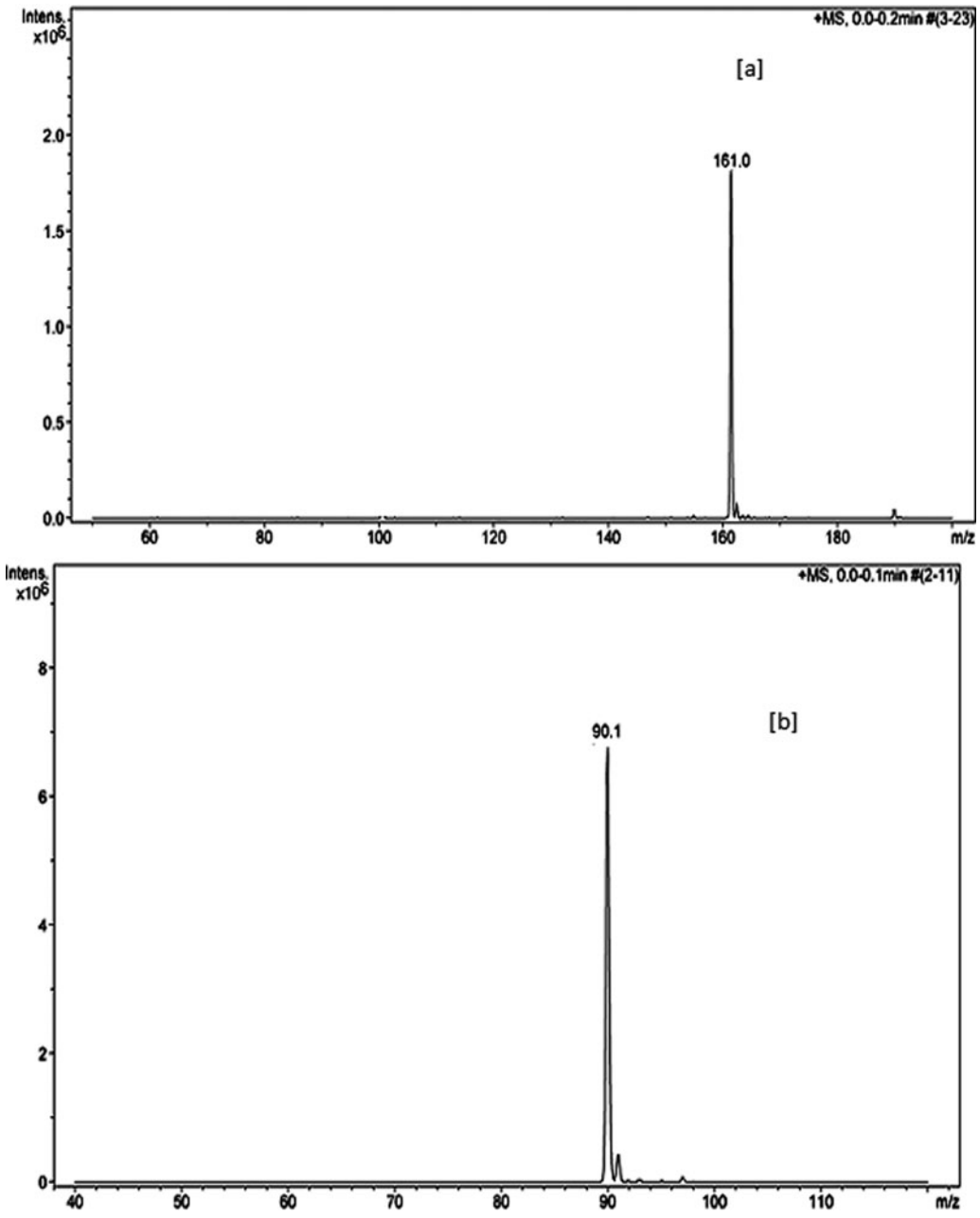

Fig. 4. ESI–MS spectra (a) alanine and (b) alanylalanine.

Both glycine and alanine resulted in the formation of peptide products on the surface of manganese oxides, but the sum product yield was higher in glycine than in alanine. Formation of peptides up to trimer was observed with glycine only whereas alanine afforded only its dimer. Table 1 reveals that glycine in the presence of MnO produced $(Gly)_3$ (16.7%) along with $(Gly)_2$ (26.8%) and cyclic$(Gly)_2$ (26.4%), while alanine produced $(Ala)_2$ (20.2%) and cyclic (Ala_2) (24.6%) after 35 days of heating at 90°C. The higher reactivity of glycine as observed can be related to its structural simplicity (Bujdak & Rode 1999a, b).

Diketopiperazine a cyclic peptides by-product identified from HPLC and ESI–MS studies was found on all manganese oxides. Its formation is favoured at higher temperatures of 120°C only (Table 1). Similar observation was made by Basiuk and Sainz-Rozas and it was postulated that the quantity of water adsorbed and hence the thickness of the hydrate layer on the metal oxide is low at higher temperatures as compared with those at ambient temperatures (Basiuk & Sainz-Rojas 2001). This further shifts the equilibrium of dehydration reactions; thus the cyclization of $(Gly)_2$ and $(Ala)_2$ into DKP seems to be more favourable at higher temperatures than the peptide chain elongation. Thus, it was natural to observe the formation of $(Gly)_3$, $(Gly)_2$, $(Ala)_2$ at lower temperature of 90°C, though the overall reaction rate was found to decrease.

The peptide yields were found to vary under different temperature conditions. For example, irrespective of the manganese oxides, temperature conditions of 90°C resulted in

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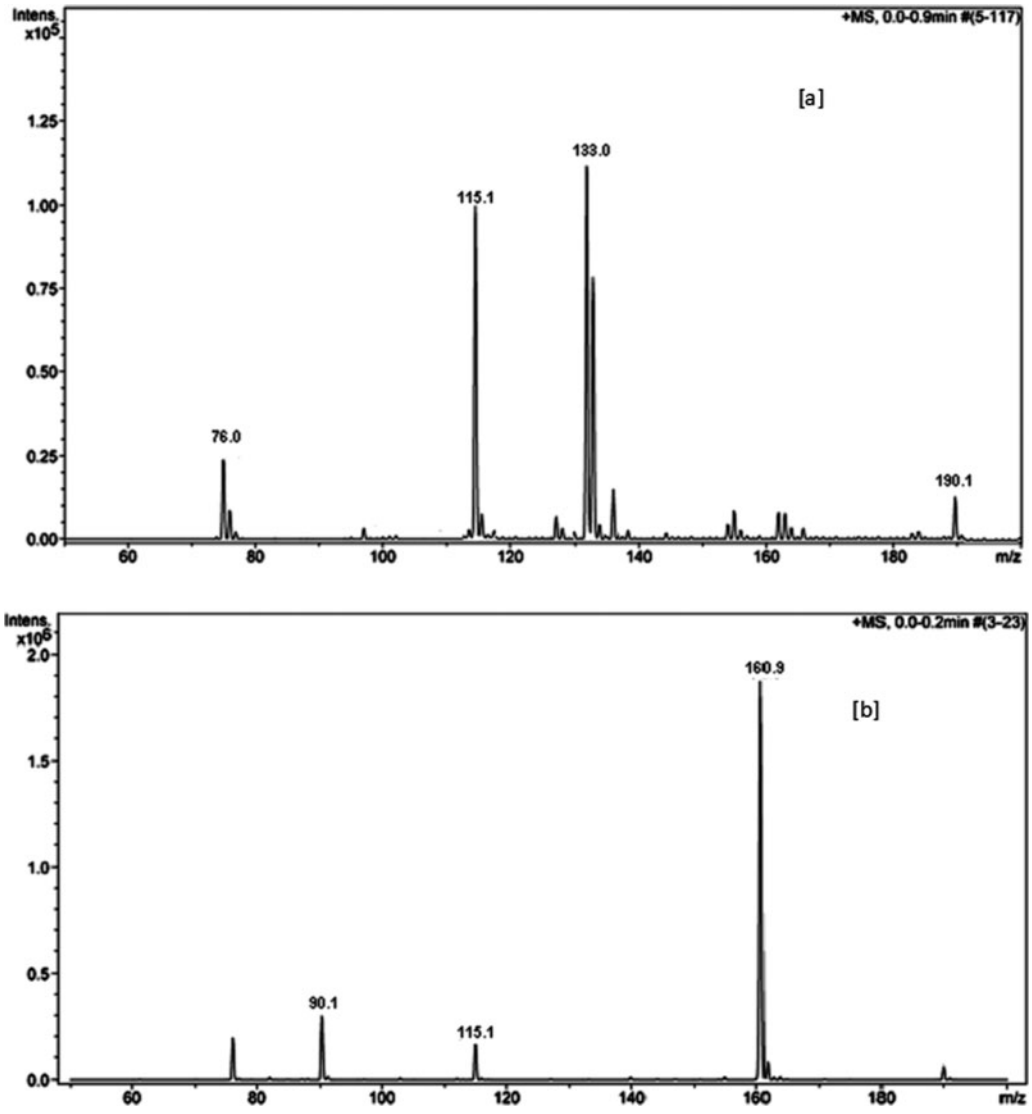

Fig. 5. ESI–MS spectra of products formed when glycine (a) and alanine (b) was heated for 35 days at 90°C in the presence of MnO.

significantly higher yields of the short peptides in comparison with those from 50 and 120°C. Trace amounts of such oligomers were also observed at 50°C. This may imply that peptide formation could have initiated at lower temperatures, but higher temperatures were required for increased yields. Basiuk & Sainz-Rozas reported similar higher oligomers yields from L-alanine on alumina (Basiuk & Sainz-Rojas 2001). Short peptide synthesis was also reported by the authors at lower temperatures of 55°C. The findings here have strong implications regarding possible environments that could have favoured prebiotic peptide synthesis. Also, time duration of 35 days were found to be sufficient for achieving highest yield of the peptides from both glycine and alanine.

It is important to note that among all the manganese oxides, MnO and Mn_3O_4 are efficient, as they produced higher yield of oligomers of amino acids in both glycine and alanine. Mn_2O_3 and MnO_2 on the other hand produced glycine and alanine oligomers in comparatively low yield. The observed yield of the products with four manganese oxides studied followed the following trend: MnO > Mn_3O_4 > Mn_2O_3 > MnO_2. Although all manganese oxides that were synthesized had nanosized particles (evidenced from Transmission Electron Microscopy studies) and more or less equal surface area (Brunauer–Emmett–Teller studies) as documented in previous studies (Bhushan *et al*. 2011), yet in the present study, highest peptide yields were obtained on the MnO surface. The results of our earlier studies have also demonstrated that manganese oxides of lower oxidation state exhibited better adsorptive potential for ribonucleotides and thus may have aided in the catalysis of various reactions necessary for the origin of life (Bhushan *et al*. 2011, 2016a, b). The early Earth had a reducing atmosphere as proposed by pioneering works of various researchers (Oparin 1938; Urey 1952; Miller 1953, 1955) and supported by works of Chyba & Sagan (1992). Thus under such conditions, manganese oxides with lower oxidation states would have been favoured. The works of Tebo prove that abiotic oxidation of Mn(II) under aerobic condition at neutral pH proceeds only at a limited rate (Tebo *et al*. 1997, 2004). On the

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other hand, the higher oxides of manganese may have formed as a result of microbial oxidation of the soluble Mn(II) in natural environments (Nealson *et al*. 1988). Hazen *et al.* further concluded that the higher oxides of manganese had no existence until the Paleoproterozoic Era when the atmospheric conditions witnessed a rise in the oxygen levels (Hazen *et al*. 2008). It can thus be concluded that manganese in its reduced form Mn(II) might have been more active during the course of chemical evolution.

Conclusion

1. All investigated manganese oxides (MnO, Mn_2O_3, Mn_3O_4 and MnO_2) are able to catalyse the production of peptide bond formation in glycine and alanine without applying cyclic drying/wetting conditions.
2. Peptide bond formation was recorded in highest yields at higher temperatures of 90°C although trace amounts are observed even at 50°C. While linear chain peptides were formed at lower temperatures, very high temperatures of 120°C favoured the formation of cyclic peptides derivatives.
3. Glycine on MnO produced cyclic $(Gly)_2$, $(Gly)_2$ and $(Gly)_3$ with alanine, cyclic $(Ala)_2$ and $(Ala)_2$ were only formed. Mn_3O_4 also produced the same products but in lesser yield, while Mn_2O_3 and MnO_2 produced least and trace mount of product of glycine and alanine.
4. The results are significant in relation to prebiotic chemistry because it has shown experimentally that manganese oxide having lower metal oxygen ratio have maximum tendency to concentrate and condense to bring about polymerized products.

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References

Amend, J.P. & Shock, E.L. (2000). Thermodynamics of amino acid synthesis in hydrothermal systems on the early Earth. Oxford University Press, pp. 23–40.

Arora, A.K. & Kamaluddin (2007). *Colloids Surf. A: Physicochem. Eng. Aspects* **298**, 186–191.

Arora, A.K. & Kamaluddin (2009). *Astrobiology* **9**, 165–171.

Arora, A.K., Tomar, V., Aarti, N., Venkateswararao, K.T. & Kamaluddin (2007). *Int. J. Astrobiol*. **6**, 267–271.

Basiuk, V.A. & Sainz-Rojas, J. (2001). *Adv. Space Res*. **27**, 225–230.

Basiuk, V.A., Gromovoy, T.Yu., Golovaty, V.G. & Glukhoy, A.M. (1991). *Orig. Life Evol. Biosph*. **20**, 483–498.

Bhushan, B., Shanker, U. & Kamaluddin (2011). *Orig. Life. Evol. Biosph*. **41**, 469–482.

Bhushan, B., Nayak, A. & Kamaluddin (2016a). *Orig. Life Evol. Biosph*. **46**, 203–213.

Bhushan, B., Nayak, A. & Kamaluddin (2016b). *Int. J. Astrobiol*. 1–13. doi: 10.1017/S1473550416000203.

Brack, A. & Barbier, B. (1990). *Orig. Life Evol. Biosph*. **20**, 139–144.

Bujdak, J. & Rode, B.M. (1996). *J. Mol. Evol*. **43**, 326–333.

Bujdak, J. & Rode, B.M. (1997a). *J. Mol. Evol*. **45**, 457–466.

Bujdak, J. & Rode, B.M. (1997b). *React. Kineto Catal. Lett*. **62**, 281–286.

Bujdak, J. & Rode, B.M. (1999a). *J. Mol. Catal. A* **144**, 129–136.

Bujdak, J. & Rode, B.M. (1999b). *Orig. Life Evol. Biosph*. **29**, 451–461.

Bujdak, J. & Rode, B.M. (2001). *Amino Acids* **21**, 281–291.

Bujdak, J. & Rode, B.M. (2002). *J. Inorg. Chem*. **90**, 1–7.

Chen, J., Lin, J.C., Purohit, V., Cutlip, M.B. & Suib, S.L. (1997). *Catal. Today* **33**, 205–214.

Chen, X., Shen, Y.F., Suib, S.L. & O'Young, C.L. (2001). *J. Catal*. **197**, 292–302.

Chyba, C. & Sagan, C. (1992). *Nature* **355**, 125–132.

Cleaves, H.J., Aubrey, A.D. & Bada, J.L. (2009). *Orig. Life Evol. Biosph*. **39**, 109–126.

Coyne, L.M. (1985). *Orig. Life Evol. Biosph*. **15**, 161–206.

Espinal, L., Suib, S.L. & Rusling, J.F. (2004). *J. Am. Chem. Soc*. **126**, 7676–7682.

Flegmann, A.W. & Scholefield, D. (1978). *J. Mol. Evol*. **12**, 101–112.

Fuchida, S., Masuda, H. & Shinoda, K. (2014). *Orig. Life Evol. Biosph*. **44**, 13–28.

Getz, W.M. (1990). *Bio Systems* **24**, 177–182.

Graf, G. & Laganly, G. (1980). *Clays Clay Miner*. **28**, 12–18.

Greenland, D.J., Laby, R.H. & Quirk, J.P. (1962). *Trans. Faraday Soc*. **58**, 829–841.

Greenland, D.J., Laby, R.H. & Quirk, J.P. (1965a). *Trans. Faraday Soc*. **61**, 2013–2023.

Greenland, D.J., Laby, R.H. & Quirk, J.P. (1965b). *Trans. Faraday Soc*. **61**, 2024–2035.

Hazen, R.M., Papineau, D., Bleeker, W., Downs Robert, T., Ferry John, M., McCoy Timothy, J., Sverjrjensky Dimitri, A. & Yang, H. (2008). Mineral evolution. *Am. Miner*. **93**, 1693–1720.

Heiserman, D.L. (1992). *Exploring Chemical Elements and their Compounds*. Blue Ridge Summit, PA Libraries, Australia.

Huber, C. & Wächtershäuser, G. (1998). *Science* **281**, 670.

Huber, C., Eisenreich, W., Hecht, S. & Wächtershäuser, G. (2003). *Science* **301**, 938–940.

Imai, E., Honda, H., Hatori, K., Brack, A. & Matsuno, K. (1999). *Science* **283**, 831–833.

Kijlstra, W.S., Brands, D.S., Smit, H.I., Poels, E.K. & Bliek, A. (1997). *J. Catal*. **171**, 219–230.

Kunin, V. (2000). *Orig. Life Evol. Biosph*. **30**, 459–466.

Lahav, N. (1994). *Heterog. Chem. Rev*. **1**, 159–179.

Lahav, N., White, D. & Chang, S. (1978). *Science* **201**, 67–69.

Lemke, K., Rosenbauer, R.J. & Bird, D.K. (2009). *Astrobiology* **9**, 141–145.

Marshall-Bowman, K., Ohara, S., Sverjensky, D.A., Hazen, R.M. & Cleaves, H.J. (2010). *Geochem. Cosmochim. Acta* **74**, 5852–5861.

Matrajit, G. & Blanot, D. (2004). *Amino Acids* **26**, 153–161.

Miller, S.L. (1953). *Science* **117**, 528–529.

Miller, S.L. (1955). *J. Am. Chem. Soc*. **77**, 2351–2361.

Nealson, K.H., Tebo, B.M. & Rosson, R.A. (1988). *Adv. Appl. Microbiol*. **33**, 279–318.

Oparin, A.I. (1938). *The Origin of Life*. Macmillan, New York.

Porter, T.L., Eastman, M.P., Hagerman, M.E., Price, L.B. & Shand, R.F. (1998). *J. Mol. Evol*. **47**, 373–380.

Qi, G. & Yang, R.T. (2003). *Appl. Catal. B: Environ*. **44**, 217–225.

Radhakrishnan, R. & Oyama, S.T. (2001). *J. Catal*. **2**, 282–290.

Rimola, A., Tosoni, S., Sodupe, M. & Ugliengo, P. (2006). *Chem. Phys. Chem*. **7**, 157–163.

Rimola, A., Sodupe, M. & Ugliengo, P. (2007). *J. Am. Chem. Soc*. **129**, 8333–8344.

Rode, B.M. (1999). *Peptides* **20**, 773–786.

Rode, B.M., Son, H.L., Suwannachot, Y. & Bujdak, J. (1999). *Orig. Life Evol. Biosph*. **29**, 273–286.

Schreiner, E., Nair, N.N., Wittekindt, C. & Marx, D. (2011). *J. Am. Chem. Soc*. **133**, 8216–8226.

Shanker, U., Bhushan, B., Bhattacharjee, G. & Kamaluddin (2011). *Astrobiology* **11**, 225.

Shanker, U., Bhushan, B., Bhattacharjee, G. & Kamaluddin (2013). *Orig. Life Evol. Biosph*. **42**, 31–45.
Shock, E.L. (1992). *Geochim. Cosmochim. Acta* **56**, 3481–3491.
Smith, J.V. (1998). *Proc. Natl. Acad. Sci. USA* **95**, 3370–3375.
Tebo, B.M., Ghiorse, W.C., Van Waasbergen, L.G., Siering, P.L. & Caspi, R. (1997). *Rev. Miner*. **35**, 225–266.
Tebo, B.M., Bargar, J.R. & Clement, B. (2004). *Annu. Rev. Earth Planet. Sci*. **32**, 287–328.
Turekian, K.K. & Wedepohl, K.L. (1961). *Geol. Soc. Am. Bull*. **72**, 175–191.
Urey, H. (1952). *Proc. Natl. Acad. Sci. USA* **38**, 351–363.
Vileno, E., Zhou, H., Zhang, Q., Suib, S.L., Corbin, D.R. & Koch, T.A. (1999). *J. Catal*. **187**, 285–297.
Voigt, C.A., Kauffman, S. & Wang, Z.G. (2000). *Adv. Protein Chem*. **55**, 79–160.
Xia, G.G., Yin, Y.G., Willis, W.S., Wang, J.Y. & Suib, S.L. (1999). *J. Catal*. **185**, 91–105.
Zamaraev, K.I., Romannikov, V.N., Salganik, R.I., Wlasoff, W.A. & Khramtsov, V.V. (1997). *Orig. Life Evol. Biosph*. **27**, 325.
Zhou, H., Shen, Y.F., Wang, J.Y., Chen, X., O'Young, C.L. & Suib, S.L. (1998). *J. Catal*. **176**, 321–328.

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