fragmentary RM[3] (A993, GSI, Nagpur) of this species has been collected from the same locality and same litho-unit which has yielded the Hominid skull. *Sus namadicus* shows affinity to Lower Pleistocene Siwalik *Sus falconeri*; the species is also reported from the Upper Pleistocene Kurnool Cave deposits[18]. *S. namadicus* possesses similar characters to Middle Pleistocene Chou-Ken-Tien form *Sus lydekkeri*[19].

A single specimen (GSI Type No. 20425) of fossilized mandible of *Cuon aplinus* has been collected[20] from the litho-unit which has preserved the Hominid skull. The specimen showing M_3 absent and M_2 much reduced is somewhat intermediate between Middle Pleistocene European *C. a. priscus* and *C. a. fossilis*[21]. Though slightly larger, the Narmada form is also comparable to Middle Pleistocene Chinese *C. a. antiquus*[22,23].

Most common fossils in the Narmada valley are of Bovidae. Major members of this family, namely, *Bos namadicus* and *Bubalus palaeindicus* are reported to range from Middle Pleistocene to Lower Holocene. However, during the last two decades, a large number of collection of fossil Bovidae has been made which deserves a thorough review to make this prolific family more useful for precise biozonation. The other dominant member, *Elephas namadicus* is also considered to be of Middle Pleistocene to Lower Holocene age. But this form possibly includes two[24] or three[25] species or subspecies. On the other hand, it is again suggested that European *E. antiquus* and some Japanese forms belong to *E. namadicus*[26]. These controversies are to be resolved to understand the role of this form in biozonation. Another family, Cervidae is not very abundant in Narmada valley. An up-to-date review work or even a proper taxonomic description is lacking for this family and thus its due significance in biozonation is yet to be recognized.

Studies on lithostratigraphy, magnetostratigraphy and tephrastratigraphy reveal that Narmada *Homo erectus* is from a bed just above a formation of 0.73 Ma and at least 19 m below a layer of 74,000 BP.

Fossils belonging to Hippopotamidae, Equidae, Stegodontidae, Suidae and Canidae are mainly relied upon for biozonation of the Narmada deposits. Fossils of these families collected along with the *Homo erectus* skull or from the same geological horizons containing the skull point to a Middle Pleistocene (in all probability its lower horizon) age of the Narmada *Homo erectus*.

The discovery of Indian *Homo erectus* bridges the gap between African *H. erectus* in the west and Chinese and Javan *H. erectus* in the east and south east respectively. There is a general consensus of opinion that Afro-Asian *H. erectus* ranges in age from Lower Pleistocene to Middle Pleistocene. Indian *H. erectus* falls within this range.

1. Sonakia, A., *Rec. GSI*, 1984, **113**, 159–172.
2. Tiwari, M. P. and Bhai, H. Y., *Spl. Publ. GSI*, 1997, **46**, 41–54.
3. Rao, K. V., Chakrabarti, S., Rao, K. J., Ramani, M. S. V., Marathe, S. D. and Borkar, B. T., *Spl. Publ. GSI*, 1997, **46**, 65–78.
4. Basu, P. K., Biswas, S. and Acharyya, S. K., *Indian Miner.*, 1987, **41**, 66–72.
5. Acharyya, S. K. and Basu, P. K., *Quat. Res.*, 1993, **40**, 10–19.
6. Agrawal, D. P., Kotlia, B. S. and Kusumgar, S., Abstract, International Symposium on Palaeoclimatic and Palaeoenvironmental Changes in Asia during the last 4 Ma, P.R.L. Ahmedabad, 1986, p. 36.
7. Mishra, S. and Rajaguru, S. N., *Man Environ.*, 1993, **xviii**, 7–12.
8. Biswas, S. and Dassarma, D. C., *Rec. GSI*, 1984, **114**, 19–24.
9. Lydekker, R., *Palaeontol Indica*, 1882, **10**, 35–104.
10. Hooijer, D. A., *Zool. Verh. Liden*, 1950, **8**, 34–55.
11. Dassarma, D. C. and Biswas, S., *J. Earth Sci.*, 1977, **4** 122–136.
12. Biswas, S., *Rec. GSI*, 1988, **118**, 53–62.
13. Matthew, W. D., *Bull. Am. Mus. Nat. Hist.*, 1929, **56**, 443–447.
14. Colbert, E. H., *Trans Am. Phil. Soc.*, 1935, **NS 36**, 1–401.
15. Hooizer, D. A., *Arch. Neerl. de Zool.*, 1949, **8**, 243–263.
16. Azzaroli, A., *Pal. Ital.*, 1982, **72**, 74–97.
17. Biswas, S. and Dassarma, D. C., Proceedings of Field Conference on N/Q Boundary India 1979, 1981, pp. 15–20.
18. Pilgrim, G. E., *Palaeontol Indica*, 1926, **NS 8**, 64–65.
19. Zdansky, D., *Palaeontol Sin.*, 1928, **4**, 91–100.
20. Biswas, S. and Basu, P. K., *Spl. Publ. GSI*, 1997, **46**, 117–121.
21. Kurten, B., *Pleistocene Mammals of Europe*, Weidenfeld and Nicolson, London 1968, pp. 108–118.
22. Matthew, W. D. and Granger, W., *Bull. Am. Mus. Nat. Hist.*, 1923, **48**, 563–598.
23. Colbert, E. H. and Hooijer, D. A., *Bull. Am. Mus. Nat. Hist.*, 1953, **102**, 41–43.
24. Tripathi, C. and Basu, P. K., *J. Palaeontol. Soc. India*, 1983, **28**, 63–66.
25. Pilgrim, G. E., *Rec. GSI*, 1905, **32**, 199–218.
26. Maglio, V. J., *Trans Am.. Phil. Soc.*, 1973, NS 63, 31–50.

Received 16 March 1998; revised accepted 29 June 1998

Occurrence of amino acids in Middle-Krol stromatolites from Nainital, Kumaun Lesser Himalaya

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Geochemical studies on Middle-Krol stromatolite sample from Nainital area of Kumaun Himalayas revealed the presence of amino acids, viz. cysteine, lysine, aspartic acid, serine, glycine, threonine, α-alanine, proline, valine and phenylalanine with varying amounts of protein bound (55%) and free amino acids (45%) of the total. Absence of non-protein amino acids points to the marked biochemical relationship between Precambrian and extant organisms and their involvement in stromatolite formation.

THE Middle-Krol is a well marked horizon of the Krol Belt extending over 300 km from Solan (HP) in the west to Naini Tal in the east. Valdiya[1] and Pant & Sharma[2] have

Figure 1. Transverse and longitudinal sections of Middle-Krol stromatolites from Naini Tal locality – along Balia Nala about 5 km SSE of Naini Tal.

shown the presence of purple green shales with yellow weathering limestone showing a variety of sedimentary structures as Middle-Krol. Although stromatolites similar to the known Middle-Riphean forms in the Naini Tal syncline have earlier been reported[2] (Figure 1), existence of organic compounds in these (chemical fossils) has not been investigated so far. Presence of biomarkers like those of palmitolic acid and oleic acid in ground waters and ancient sediments of the coastal Karaikal region of Cauvery delta of Pondicherry has been reported by Verma and Sukhija[3]. Edman and coworkers[4] were able to isolate amino acids from the marine sediments. Abelson[5] found thermally stable amino acids in greater abundance in the Precambrian sediments. Harrington[6] has successfully identified several amino acids including serine in abundance in corcidolite asbestos of Precambrian age from South Africa. Amino acids were also detected in extracts from black cherts of Bitter Springs by Schopf *et al.*[7].

Amino acids and other organic compounds have been shown to exist in rocks and sediments from Gunflint Chert in Ontario (dated 2×10^9 years) and Bitter Springs Formation in Australia (dated 1×10^9 years)[8]. Mattoo and coworkers[9] have identified amino acids and fatty acids in the stromatolite sample from Someshwar area of Almora, Kumaun Himalaya. Mathur *et al.*[10] have reported the records of Ediacaran Fauna from the Krol-Belt of the Naini Tal Hills, which is believed to mark the transition from Proterozoic to Phenerozoic.

Formation of biomonomers and their oligomers similar to those found in ancient stromatolites under primordial primitive earth conditions have earlier been effected by Pathak *et al.*[11,12] and Pant[13] with the aim of retracing the pathways of their prebiotic formation leading to the origin of primitive organisms many billion years ago before Precambrian era. Presence of organic matter as biomarkers in stromatolites and sediments has earlier been shown but biological markers, particularly amino acids in Precambrian stromatolites and associated sedimentary rocks of Naini Tal area of Himalaya have not been investigated so far. Therefore, geochemical investigations on Middle-Krol stromatolites from Naini Tal syncline have been carried out and the results are reported here.

Aliquots of concentrates of aqueous extract of a portion of the finely-powdered (240 mesh size) stromatolite sample were collected from unweathered, unmetamorphosed and least deformed outcrops, repeatedly washed with sterilized pyrogen-free water and freed of volatile content by extraction with benzene–ethanol (3:1 v/v) system on unidimensional, two-dimensional circular paper, thin layer (Silica gel G 0.5 mm thickness) chromatography (Whatman No. 1 paper, solvent system BAW 4:1:1 v/v; 4:1:5 v/v upper layer, BAPW 15:3:10:12 v/v and ninhydrin as reagent)[14], UV spectroscopy and HPLC (C_{18} column; 50% water in acetonitrile flow rate 0.7 ml/min and 70% water in acetonitrile flow rate 0.4 ml/min as mobile phases monitoring the elute at 212 nm)[15]. Five amino acids, viz. cysteine, aspartic acid, α-alanine, valine and phenyl alanine were detectable. Another portion of stromatolite sample on acid hydrolysis (6N HCl for 24 h) after removal of residual acid on analysis by similar methods, revealed five more amino acids, viz. lysine, glycine, threonine, serine and proline in combined state in addition to one unidentified product[16]. The amino acids found in moderate amount were colorimetrically determined at 570 nm using Photochem colorimeter-MKIII.

UV spectra (using Beckman DK-2 spectrophotometer) of aqueous extract of unhydrolysed and hydrolysed

samples showed coincidence (R_f 16% in BAW and 33% in BAPW) with standard aspartic acid λ_{max} at 212 nm and other amino acids (R_f 17.4%, 18%, 20%, 34% and 47% in BAW and 33.5%, 35%, 45%, 54% and 70% in BAPW) showed λ_{max} at 195 nm, 190 nm, 210 nm, 214 nm and 216 nm characteristic of serine, glycine, threonine, α-alanine and valine, respectively. Sharp absorption peak λ_{max} at 260 nm (R_f 57% in BAW and 82% in BAPW) in aqueous extract was due to phenylalanine. The identity of amino acids detected in unhydrolysed and hydrolysed aqueous fractions of stromatolite (50–700 μg) was further ascertained by HPLC (SHIMADZU 221–25412 unit C_{18} column) using 50% water in acetonitrile flow rate 0.7 ml/min as well as 70% water in acetonitrile flow rate 0.4 ml/min as mobile phases and monitoring the elute continuously at 212 nm. The peak values (retention time) of the products under investigation were compared with authentic amino acid standards given in *CRC-HPLC Handbook*[17].

Intense HPLC peaks observed in aqueous extract at 5.722 min, 15.125 min and 20.558 min corresponded exactly with aspartic acid, cysteine and valine respectively, with a weak peak at 13.958 min (unidentified) in C_{18} column using 50% water in acetonitrile (flow rate 0.7 ml/min) as mobile phase and UV detector at 212 nm. However, HPLC of hydrolysed samples freed of HCl showed peaks at 4.950 min, 5.425 min, 5.775 min, 10.550 min, 11.217 min, 12.483 min, 12.483 min, 14.883 min, 20.375 min and 25.775 min. Of the observed nine peaks, at 5.775 min, 12.483 min, 14.883 min and 20.375 min were those of aspartic acid, glycine, alanine and valine respectively. On varying the concentration of mobile phase 70% water in acetonitrile with a flow rate of 0.4 ml/min at 212 nm, the new resolved peaks observed at 6.567 min, 7.355 min, 9.592 min, 38.858 min and 51.510 min were those of threonine, serine, proline, phenylalanine and lysine respectively, similar to those of authentic reference standards.

From the data it appears that in Middle Krol stromatolite, five amino acids – cysteine (traces), aspartic acid (90 μg), α-alanine (100 μg), valine (180 μg) and phenyl alanine (100 μg) were present in the free state and on acid hydrolysis five more amino acids as lysine (100 μg), serine (130 μg), glycine (100 μg), threonine (170 μg), proline (180 μg) and one unidentified product could be detected. However, the quantity of amino acid identified in the free state was moderately higher than those released on hydrolysis.

The overlying upper Krol-Tal transition also marks the Precambrian–Cambrian boundary (570 my) and a variety of shelly microfauna possibly started appearing towards the terminal phase of Krol sedimentation[18]. The presence of amino acids in the Middle Krol-stromatolite samples from Naini Tal appear to be either molecular remains of those extinct organisms thought to have formed the stromatolite under investigation or constituents of geochemically-produced peptides or proteins believed to have comprised the main matrix of terrestrial organisms. From the present data it is evident that the stromatolite of the Naini Tal Lesser Himalayan area may have been formed from organic matter of biogenic origin, probably 1350 ± 50–950 million years ago and it also provides an additional evidence of existence of ancient sediments comprised of organic matter of biogenic origin. This is a growing, hitherto unexplored field of research and represents a significant contribution to our understanding of biochemical resemblance of ancient organisms (Precambrian and Extant) evolved by way of molecular evolution from life-forming molecules. Further work in this direction is in progress and efforts are being made to understand the detailed chemostratigraphy and their isotopic composition.

1. Valdiya, K. S., *Geology and Natural Environment of Nainital Hills, Kumaun Himalaya*, Gyanodaya Prakashan, Nainital, 1988, p. 155.
2. Pant, C. C. and Sharma, A. K., *Curr. Sci.*, 1988, **57**, 608–611.
3. Verma, V. N. and Sukhija, B. S., *Curr. Sci.*, 1993, **65**, 696–703.
4. Edman, J. G., Vereti, M., Marlett and Hanson, W. E., *Science*, 1956, **124**, 1026–1027.
5. Abelson, P. H., *Carnegie Inst. Wash. Year Book*, 1954, **53**, 97–101.
6. Harrington, J. S., *Science*, 1962, **138**, 521–522.
7. Schopf, J. W., Kven Volden, K. A. and Barghoorn, E. S., *Proc. Natl. Acad. Sci. USA*, 1968, **59**, 629–636.
8. Elington, G. and Calvin, N., *Chemical Fossil Sci. Am.*, 1967, **216**, 32–43.
9. Mattoo, A. K., Shah, A. N. and Munshi, S. K., *Curr. Sci.*, 1979, **48**, 623–624.
10. Mathur, V. K. and Shanker, R., *J. Geol. Soc. India*, 1989, **34**, 245–254.
11. Pathak, C. K., Pant, J. N. and Pathak, H. D., *Br. Interplanet. Soc. London*, 1978, **33**, 103–106.
12. Pathak, C. K., Ph D thesis, Kumaun University, Naini Tal, 1979.
13. Pant, C. K., *Chem. Ed. UGC Res. J. India*, 1990, **7**, 14–23.
14. Hais, I. M. and Macke, K., *Paper Chromatography*, Academic Press, New York, 1963, pp. 437–494.
15. Grenstein, J. P. and Wintz, N., *Chemistry of Amino Acids*, John Wiley & Sons, New York, 1961, vol. 3.
16. Robinson, W. E., *Organic Geochemistry*, Springer-Verlag, Berlin, 1969, p. 191.
17. Hancock, W. S. and Harding, D. R. K., *CRC Handbook of HPLC for Separation of Amino Acids, Peptides and Proteins*, 1982, vol. I, pp. 114–116 and 235–246.
18. Kumar, G., International Geological Correlation Programme (IGCP) Project, 1984, p. 29.

ACKNOWLEDGEMENTS. We thank the authorities of the Departments of Chemistry, Geology, DSB Campus, Kumaon University, Naini Tal, for providing necessary research facilities and the University Grants Commission, New Delhi, for financial support. We also thank Mr G. C. Melkani, CDRI, Lucknow, for spectral and HPLC analysis.

Received 6 October 1997; revised accepted 23 June 1998