

Himalaya¹⁶. Palaeomagnetic studies also support such an interpretation. Recent palaeomagnetic data¹⁷ for the northwestern Himalaya put the time of the India-Asia collision at ~60 Ma or even close to the K/T boundary as supported by palaeontological evidence for some link between India and Asia at that time^{18,19}. Palaeomagnetic data for the eastern Himalaya demonstrate later collision at 45-50 Ma²⁰.

Assuming an early collision of the Indian plate on its northwestern margin close to the K-T boundary, an interesting point emerges from Figure 2. The peak of hornblende ages at 35-45 Ma for the northwestern Himalaya indicates that crustal thickening associated with the collision and subsequent thermal acme of the regional metamorphism were reached shortly after the collision. This interpretation has been given for the Indian plate crystalline stack in the Pakistan Himalaya²¹. The hornblende ages we report here for the HHC rocks in Zaskar agree with such a thermal history and can be explained considering the very fast drift of the Indian plate during the Cretaceous (18-20 cm/yr compared to the present rate of 4-5 cm/yr) and the substantial decrease in the drift rate during early Tertiary^{17,20}.

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Ornithoid eggshells from Deccan intertrappean beds near Anjar (Kachchh), Western India

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We describe here the ornithoid eggshell fragments from the Deccan intertrappean beds (Late Cretaceous) near Anjar, district Kachchh, Gujarat. The find assumes palaeobiogeographic significance as morphologically similar eggshells are known from the Late Cretaceous Nemegt Formation of Mongolia. Taxonomic affinities (dinosaurian/avian) of these eggshells cannot be established at present.

DOCUMENTATION of dinosaur (sauropod) egg clutches from Late Cretaceous Lameta Formation of central and

western India has increased considerably in recent years¹⁻⁵. However, the record of ornithoid (or avian-like⁶) eggshells was so far restricted to Pleistocene deposits where they have been referred to the ostrich *Struthio* cf. *S. asiaticus*⁷. Here we describe such eggshells from the Deccan intertrappean beds at a locality about 1.5 km SE of the village Viri (23° 4' 50" N: 70° 30' E) near Anjar, district Kachchh, Gujarat (Figure 1). This record, of which a brief mention was recently made⁸, follows the discovery of dinosaur bones in the same general area⁹.

The eggshell-yielding bed comprises dark grey splintery shale containing stringers of chert. In the local flow stratigraphy⁹, it occurs between the third and fourth lava flows, representing the third intertrappean level in the area (Figure 1). Screen-washing of these shales yielded a diverse assemblage of eggshell fragments including those of sauropod dinosaurs and geckonid lizards, besides the most abundant ornithoid

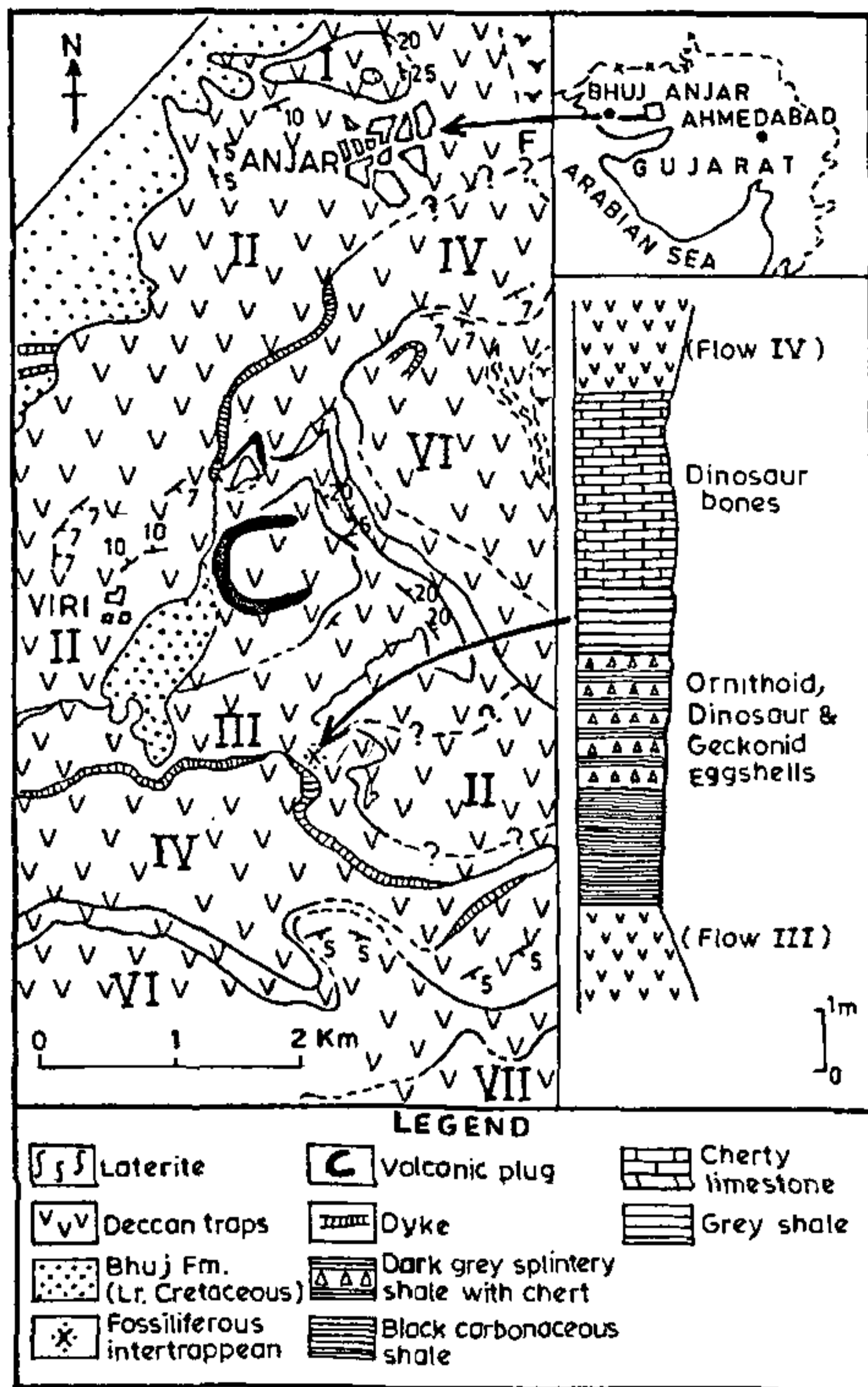


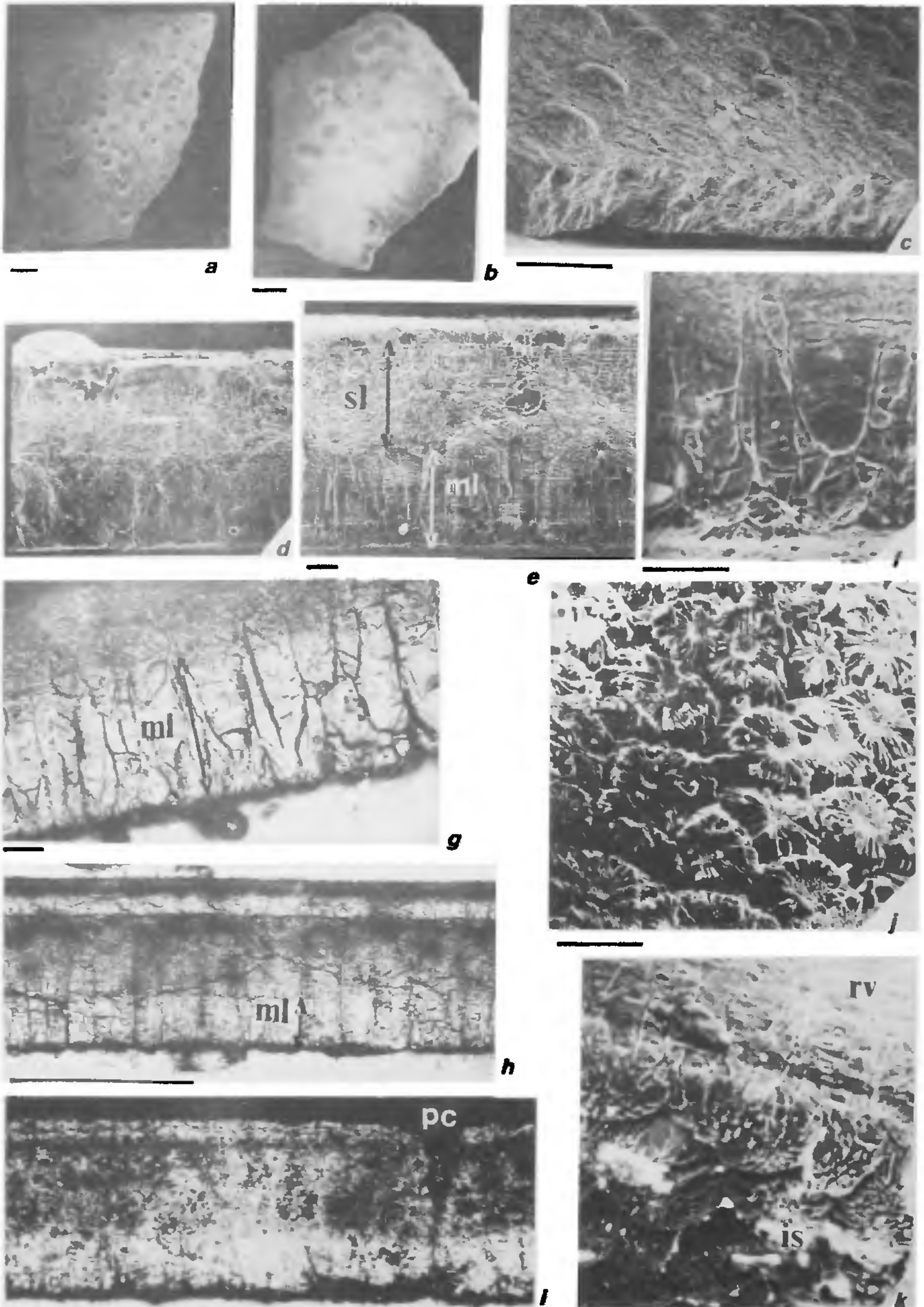
Figure 1. Geological map of the Anjar area and lithostratigraphic section at the collecting locality (map from Ghevariya, 1988).

eggshells. In addition, isolated theropod tooth, fishes including dasyatids, percoid otoliths, microlamelli-branches and gastropods were recovered from this lithounit. Fragmentary dinosaur bones occur at the top of this intertrappean sequence in the area⁸⁻¹⁰. The assemblage suggests a Late Cretaceous (Maastrichtian) age based on correlation with similarly dated dinosaur-bearing intertrappeans of western Kachchh, Nagpur, Asifabad and Jabalpur^{5,8,11,12}. The contrary suggestion of an Early Palaeocene age¹⁰ for the third intertrappean sequence (ornithoid eggshell bearing) is not tenable in the absence of data on palynofossil assemblages, absolute ages (⁴⁰Ar-³⁹Ar) and palaeomagnetic measurements from Anjar. Also, the reported presence of ornithischian eggs and clutches in the second intertrappean level in the area¹⁰ remains unconfirmed as no details of these eggs are as yet published.

The present eggshell sample consists of about 300

fragments of which the largest measures about 30 mm². No complete egg has as yet been found. The thickness of these eggshells varies between 0.35 mm and 0.45 mm excluding a thin secondary deposit present on most fragments. Their outer surface is characterized by irregularly spaced, isolated tubercles with no distinct orientation, although clusters of 2 or more tubercles are also found in some fragments (Figure 2a, b). In radial thin sections (Figure 2g-i), the presence of two layers, an inner mammillary layer and an outer spongy layer (or continuous/single layer), is clearly seen. The mammillary layer varies in thickness from one-third to slightly less than one-half of the total shell thickness. It consists of tightly packed, slender mammillary cones with radiating crystallites. The spongy layer is well differentiated from mammillary layer but shows no well-defined structural pattern. Consequently, shell units are distinct only in the mammillary layer. Viewed under SEM (Figure 2d-f) the mammillary layer consists of petal-like crystalline structures rising from the mammillary core. The spongy layer lacks any well-defined pattern but in rare instances, it shows some faintly developed columnar structures. In one instance, widely spaced horizontal layering (? growth striations) was observed (Figure 2e). No pores were found on the outer surface. In radial sections also, no pore canal could be seen except in one instance (Figure 2i) where a short, nearly straight canal tapering inwards was found. In configuration, it appears to correspond to the angusticanalicate type of pore pattern^{13,14}. The inner surface is diagenetically altered in most cases and consists of coarse crystalline structure. In a few instances, however, it shows excellently preserved mammillary knobs (Figure 2j, k). These are circular or polygonal in shape and are tightly packed with negligible intermammillary spaces. The mammillae vary in diameter from 0.03 mm to 0.05 mm and in a majority of cases (where preserved) they are cratered.

The ever-increasing documentation of Late Cretaceous eggshells from peninsular India makes it necessary to classify the known material in a manner which would reflect the variability of various structural parameters of eggshells. Recently, we¹⁵ have distinguished five eggshell types collectively from the Lameta Formation and intertrappean beds. Three of these, designated as (?)TST-I, (?)TST-II, (?)TST-III, are attributable to titanosaurid dinosaurs, although the evidence of embryonic remains or hatchlings is still awaited. Of these, (?)TST-I and (?)TST-III are exemplified by the eggshell material from Kheda² described as Kheda Type A and Kheda Type B respectively. The fourth eggshell type (Indet. Dinosauria) also shows sauropod-like shell units but is extremely thin (less than 0.4 mm). Such eggshells were first described from Asifabad intertrappeans¹⁶. A recent record¹⁷ from the Lameta Formation of Nand area is probably referable to the



same category, although detailed description and illustrations of the Nand eggshells have yet to be published.

The ornithoid eggshells described here constitute the fifth eggshell type known from peninsular Cretaceous sequences. These eggshells can easily be assigned to Ratite morphotype¹⁸ in which the shell structure is characterized by two layers (mammillary and spongy layers) and the shell units are discrete only in the mammillary layer. Elsewhere in the world the Cretaceous records of such eggshells are mainly known from Mongolia, China and Kazakhstan and a number of *parataxa* have been proposed to classify them¹⁸. Originally, these avian-like eggshells were described as 'angusticanaliculate' type and were sought to be related to ornithischian dinosaurs^{6,13}, an interpretation later supported by other workers¹⁴. On the other hand, a more recent viewpoint¹⁸ favours taxonomic attribution of part of the angusticanaliculate eggshell material (family Elongatolithidae) from Mongolia and China to theropod dinosaurs. Judging from illustrations, these eggshells are distinguishable from the Anjar material in the details of surface sculpture and in being thicker (maximum by over 4 times). Similarly, the ornithoid-ratite eggshells (? *Troodon*) reported from the Upper Cretaceous (Campanian) Two Medicine Formation of Montana¹⁹, can be distinguished from the present specimens in being much thicker (average thickness 1–2 mm), in having a considerably thinner mammillary layer (1/10 to 1/12 of shell thickness) and in a pronounced change from the mammillary to spongy layer. In these respects the 'avian-like' eggshells from Montana¹⁹ compare favourably with the Anjar eggshells, although they have a smooth outer surface.

The Anjar eggshells compare most closely with the two new ornithoid families, *Laevisolithidae* and *Subtiliolithidae*, recently described from the Late Cretaceous Nemegt Formation of Mongolia¹⁸. However, the outer surface of *Laevisolithid* eggshells is smooth and the mammillary layer in the family *Subtiliolithidae* is 2 to 3 times as thick as spongy layer.

In conclusion, the ornithoid eggshells from Anjar probably represent one of the two above-mentioned *parataxa* from Mongolia, or a closely related group. Taxonomic assignment of these eggshells can be made only after embryonic remains or hatchlings are found. As of now, this find is significant not only in terms of

enhancing the diversity of Late Cretaceous eggshell record from India but possibly also because it further emphasizes the now well-established Asiatic character of intertrappean biotas²⁰.

Repository: The material is stored in Vertebrate Palaeontology Laboratory, Department of Geology, Panjab University, Chandigarh.

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Figure 2. Ornithoid eggshells. a–c, outer surface (SEM); d, e, radial views (SEM, fractured surface); f, enlarged mammillary cones (SEM); g–i, radial thin sections; j, inner surface (SEM); k, inner surface and lower part of radial section (SEM). Bar equals 500 µm for a–c, f and 50 µm for d–g, j, k. Abbreviations: is, inner surface; ml, mammillary layer; pc, pore canal; rv, radial view; sl, spongy layer.

Structural analyses of β -amino acid containing peptides

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Unnatural amino acids (such as β -amino acids) are useful research tools in peptide chemistry. We present conformational energy calculations using molecular mechanics (MM2) on two model compounds containing β -amino acid derivatives. The low energy models are characterized by a lack of intramolecular hydrogen bonding interactions, qualitatively consistent with the results of the IR studies. X-ray crystal structures of β -amino acid-containing compounds lie within 3 kcal/mole of the global minimum model. Stereochemical guidelines for the incorporation of β -peptide residues have been proposed.

PEPTIDES are one of the most widely studied class of compounds in the course of drug discovery. Endogenous peptides, with well-characterized physiological receptors, have been recognized as vital biological effectors such as hormones and neurotransmitters¹. As peptide-based drugs suffer from the disadvantage of poor oral bioavailability², a variety of strategies to design peptidomimetics has evolved to provide enhanced metabolic stability without any loss of biological activity³⁻⁶. Somatostatin and LHRH analogs exemplify such strategies^{3, 7}.

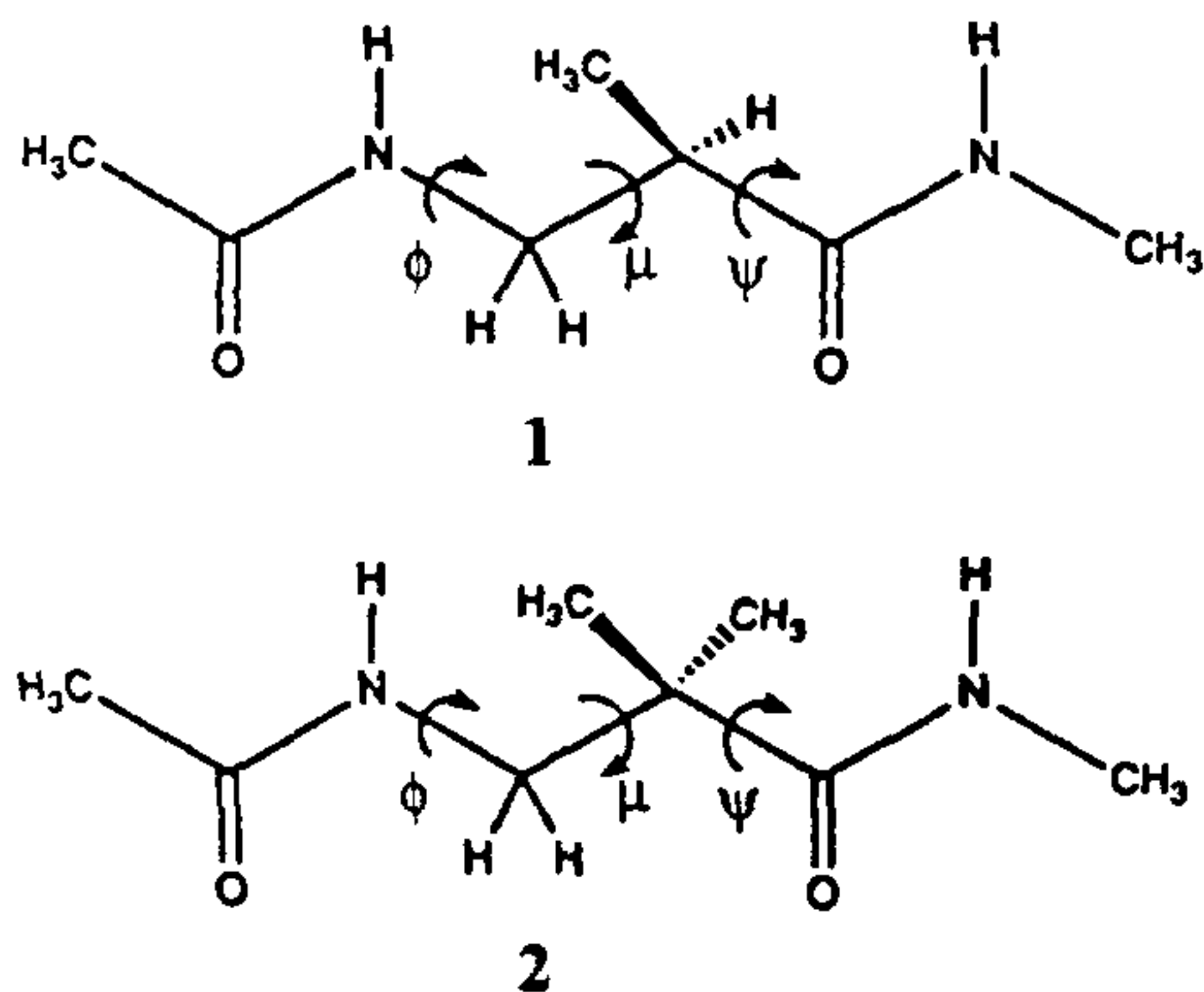


Figure 1. Schematic representation of model compounds 1 and 2 and the definition of the three conformational parameters, ϕ , μ and ψ . The three torsions are defined along the 'backbone' of the pseudopeptides 1 and 2 as [ϕ (C-N-C α -C β); μ (N-C α -C β -C); ψ (C β -C α -C-N)].

Here, we present modifications to peptide structures by replacing an α -amino acid by a β -amino acid derivative (α -methyl- β -alanine; AMBA) 1 and 2 (Figure 1). Crystallographic data on β -peptides are limited⁸⁻¹⁴. IR studies have provided some insights into intramolecular hydrogen bonding preferences in β -amino acid-containing compounds^{8, 15}. We have used the methods of molecular mechanics to understand the energetic preferences of various conformations of 1 and 2. Our results are qualitatively consistent with the crystallographic and IR observations.

The pseudopeptides 1 and 2 were model-built in an extended conformation using MacroModel (v.3.0) (ref. 16) and energy-minimized using MM2¹⁷ at a dielectric constant of 4.0. The minimized models were then used to generate conformations as a function of ϕ , μ and ψ varied at 30° intervals from 0° to 360° and optimized in two stages. First, ϕ , μ and ψ were constrained to their starting values with a harmonic force constant of 1000 kcal/mole², while the rest of the structures were allowed to energy optimize in cartesian space. In the second stage, the output of the first stage was optimized by allowing all degrees of freedom to move. The resultant sets of energy minima for 1 and 2, are designated as S1 and S2, respectively.

The collections of unique structures for 1 and 2 were analysed for the distributions of ϕ , μ and ψ . Two of these with most widespread distributions were then chosen to carry out further conformational energy calculations by their systematic variations at 10° intervals, ranging from 0° to 360°. During such calculations, the two torsions were constrained as above while no constraints were placed on the third angle. The conformational energy calculations on 1 were carried as a function of ϕ and μ , while the corresponding calculations for 2 were done as a function of μ and ψ , for reasons stated in the later text (*vide supra*).

All the energy calculations were done on the Silicon Graphics 4D/240 GT at Searle consuming a total of about 12 hours of CPU time for both the molecules. The processing of data was done through the program CONMAP (written by one of us, VNB) which took about 3 minutes on a VAX8650.

Set S1 has eleven structures (Table 1), which are all within 1 kcal/mole of the global minimum (Figure 2). The torsion ψ has only two sets of values, one centered around -60° and the other around 180°. The torsion ϕ also has only two sets of values, but their ranges are larger than that of ψ . μ varies over the three standard ranges centered around $\pm 60^\circ$ and 180°. Hence, conformational energy calculations on 1 were carried out as a function of ϕ and μ while keeping ψ around -60° and 180°. Tables 3 and 4 list the energy minima in these calculations starting with the global minima.