Distribution, stereochemistry, and stable isotope composition of amino acids in K/T boundary sediments

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Abstract

The Cretaceous/Tertiary (K/T) boundary, with an age of 65 million years before present, is associated with the mass extinctions of dinosaurs and other terrestrial and marine organisms. Evidence for the K/T boundary is reported in both marine and non-marine stratigraphic units. The presence of two exotic amino acids, α-aminoisobutyric acid and isovaline, has been reported from Stevns Klint, Denmark sediments. Two hypotheses have been proposed for the occurrence of α-Aiba and I-val in the Stevns Klint sediments: (1) they are of extraterrestrial origin; and (2) they are the by-products of the thermal alteration of coal. To test these hypotheses, samples were obtained from three K/T boundary sites, two (Starkville South and Raton Pass) located in the non-marine Raton Basin of Colorado and New Mexico and one from the marine sequence at Stevns Klint, Denmark. The samples were analyzed for amino acid distributions and stereochemistry, bulk stable C and N isotope compositions and stable C isotope compositions of individual amino acids at the Starkville South site. Protein and non-protein amino acid components are present in the K/T boundary sediments at nmol/g levels and are primarily of the L-configuration. The non-protein amino acids, α-Aiba and I-val, were detected in several of the sediment samples based on retention times and verified through coinjections of authentic standards. Protein and non-protein amino acid components of the Murchison meteorite are enriched in ^{13}C relative to terrestrial materials. The $\delta^{13}C$ values of individual amino acids in the Starkville South samples are, however, depleted in ^{13}C in all samples, with values ranging from $-13‰$ for glycine to $-31‰$ for L-isoleucine. In contrast, the $\delta^{13}C$ value for glycine in Murchison is $+22‰$. Also, bulk organic $\delta^{13}C$ and $\delta^{15}N$ values for the K/T boundary sediments are substantially depleted in ^{13}C and ^{15}N relative to bulk values for the Murchison meteorite. It is therefore suggested that the amino acids in these K/T boundary sediments are primarily of terrestrial, biogenic origin. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: KT boundary sediments; Amino acid distribution; Amino acid stereochemistry

1. Introduction

The end of the Cretaceous period, approximately 65 million years ago, is associated with the mass extinction of dinosaurs and other terrigenous fauna and flora (e.g. Jiang and Gartner, 1986; Keller, 1988; Brinkhuis and Zachariasse, 1988; McKinnon, 1992). Considerable reductions in marine, calcareous plankton and tropical invertebrates also occur at this time in the fossil record

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(e.g. Keller, 1988; Brinkhuis and Zachariasse, 1988; Meyers, 1992a). These mass extinctions identify a sharp, worldwide boundary separating the Cretaceous from the Tertiary.

Stratigraphic evidence for the Cretaceous/Tertiary (K/T) boundary are seen in marine (Zhao and Bada, 1989; Wolbach et al., 1990; Thierstein et al., 1991; Meyers, 1992a) and non-marine sediments (Gilmore et al., 1984; Schimmelmann and DeNiro, 1984; Nichols, 1990). Marine sequences found in Denmark, Italy and New Zealand led to a global search for other such sites (Nichols, 1990). Various marine sequences were located around the world but only in western North America have non-marine sections been located (Nichols, 1990). The boundary layer is identified, in all instances, by the abrupt disappearance of the regional uppermost Cretaceous palynoflora at the level of an iridium (Ir) anomaly (Nichols, 1990). At many of the boundary sites shock-metamorphosed minerals (Hallam, 1989; Alvarez et al., 1989; Nichols, 1990; Hildebrand et al., 1991; Sharpton et al., 1992), nanometer-sized diamonds (Carlisle and Braman, 1991; Carlisle, 1992; Gilmour et al., 1992), and soot and charcoal (Wolbach et al., 1988; Gilmour et al., 1989; Wolbach et al., 1990) have also been reported.

The nature and cause of the late Cretaceous extinctions have been the focus of heated arguments between gradualists and catastrophists (e.g. Upchurch, 1989). A primary change of the physical environment at the end of the Cretaceous, in which species that were adapted to a warmer climate and shallow marine habitats were most affected, is typical of all mass extinction scenarios (Upchurch, 1989).

The most commonly proposed causes of extinction by gradualists are long term global cooling, major marine regression (Officer and Drake, 1983, 1985; Stanley, 1984, 1987; Upchurch, 1989) and acid rain as a component of the recent 'volcanic winter' hypotheses (Officer et al., 1987). Stanley (1984) suggested that the well-documented, late Cretaceous period shows patterns that also appear in previous marine mass extinctions. A period of climatic cooling occurred during this period, and the extinctions were not instantaneous but covered more than 10^6 years (Stanley, 1984).

Other authors have suggested that this period of climatic cooling could be due to increased vulcanism (e.g. Gledhill, 1985) or global marine regression (e.g. Kauffman, 1984). However, in recent years, studies have indicated that the seas were not receding at the end of the Cretaceous (Stanley, 1984) and leaf megafloras from the southern Rocky Mountains show no indication of climate cooling near the K/T boundary (Upchurch, 1989).

Most catastrophic extinction scenarios have been attributed to a large bolide impacting the Earth (Alvarez, 1986; Grieve, 1989; Alvarez and Asaro, 1990; Hildebrand et al., 1991) or a massive series of volcanic eruptions (Hallam, 1989; Courtillot, 1990) at the end of the Cretaceous. Either of these scenarios could account for short-term global cooling, cessation of photosynthesis, acid rain and extensive wild-fires as the major components of the extinction process (Upchurch, 1989; Alvarez and Asaro, 1990). Strong disagreements exist in the scientific community over the impact versus volcanic extinction scenarios. Both of these hypotheses could account for the high abundances of Ir, shocked quartz grains and chemical components found at the boundary (Courtillot, 1990). A large, buried impact crater, called the Chicxulub crater, measuring 170–200 km in diameter, has been recently discovered on the Yucatan Peninsula of Mexico (Pope et al., 1991; Hildebrand et al., 1991; McKinnon, 1992; Sharpton et al., 1992). This crater is believed by many to be the location of the impact suggested to have initiated the K/T boundary mass extinctions (Pope et al., 1991). Massive volcanism was also taking place at the end of the Cretaceous, principally in what is today, the Deccan Traps of India (Courtillot, 1990).

Several studies have been conducted on trace element distributions above, at and below the K/T boundary. An Ir anomaly has been confirmed at each of the K/T boundary sites studied (e.g. Gilmore et al., 1984; Zhao and Bada, 1989). At Raton Basin, Colorado and at Stevns Klint, Denmark the Ir concentrations reach 56 ppb (Gilmore et al., 1984) and 87 ppb (Zhao and Bada, 1989), respectively. Iridium is rarely found in the Earth's crust because most of the iridium is complexed with iron in the core. The average Ir level in the

crust is 0.03 ppb, whereas carbonaceous meteorites contain approximately 500 ppb (Alvarez and Asaro, 1990). At Raton Basin, all sites have a 2–4 cm kaolinitic-rich clay layer overlain by coal in association with the Ir anomaly and the disappearance of the *Proteacidites* pollen taxon (Gilmore et al., 1984). The anomaly in the Raton Basin reaches its maximum concentration, not in the thin kaolinitic boundary layer, but rather in a coal layer just above the boundary clay (Gilmore et al., 1984). At the Stevns Klint location, the Ir anomaly is identified at the boundary itself (Zhao and Bada, 1989). However, sampling conducted at the Stevns Klint site was of much lower resolution than that at the Raton Basin sites. Few published organic geochemical studies have been conducted on sediments above and below the K/T boundary. The studies that have been published include: the characterization of organic matter from seven locations, all of which were marine environments at the K/T boundary (El Kef, Tunisia; Negev Desert, Israel; Stevns Klint, Denmark; Brazos River, Texas; Deep Sea Drilling Project Sites 577 and 605 and Ocean Drilling Project Site 761), using Rock-Eval pyrolysis and distributions of extractable biomarkers (Meyers and Simoneit, 1990).

Suites of K/T boundary sediments have been analyzed from the Morena Formation of California; various Deep Sea Drilling Project (DSDP) sites and the locations mentioned above for organic carbon and carbonate carbon contents (Schmitz et al., 1988; Meyers and Simoneit, 1990; Meyers, 1992b). These analyses indicated that organic carbon contents are low, ($0.01–0.95\%$ C_{org}), whereas the inorganic carbon contents are quite varied ($2–94\%$ $CaCO_3$; Meyers and Simoneit, 1990).

Analysis of extractable biomarkers at the K/T boundary indicated that microbial reworking of organic matter was extensive (Meyers and Simoneit, 1990). The hydrocarbon distributions of some sample sets, such as Stevns Klint, Denmark, show the absence of *n*-alkanes and the predominance of anteiso-alkanes, with a minor contribution of other branched alkanes (Meyers and Simoneit, 1990). Although other sample sets closer to the continental margin, such as some of

the DSDP cores from the North Atlantic, show significant abundances of *n*-alkanes (which are indicative of waxes of land plants with carbon chain lengths of C_{27}, C_{29} and C_{31}), the amounts of these compounds are greater in the late Cretaceous samples than in similar samples from the early Tertiary (Meyers and Simoneit, 1990). Samples from DSDP Site 605, on the New Jersey continental margin, contain terrigenous inputs and have pristane/phytane values greater than one in the late Cretaceous samples and less than one in the early Tertiary samples. These lower values in the Tertiary sediments could suggest greater activity by methanogenic bacteria and possibly less reworking of the organic material than was indicated in the Cretaceous sediments (Meyers and Simoneit, 1990).

Marine and non-marine K/T boundary sites have been analyzed for organic carbon (e.g. Schimmelmann and DeNiro, 1984; Magaritz, 1989; Meyers and Simoneit, 1990; Meyers, 1992b), nitrogen and hydrogen stable isotopes (Schimmelmann and DeNiro, 1984). Schimmelmann and DeNiro (1984) reported a shift of 1.8‰ to more depleted organic $\delta^{13}C$ values just above the K/T boundary at York Canyon, Raton Basin, New Mexico. A similar ^{13}C depletion of 0.5‰ (Zachos and Arthur, 1986) to 3.3‰ (Hsu et al., 1982) has been identified for marine sediments, indicating a worldwide reworking of the carbon cycle (Zachos and Arthur, 1986). Minor fluctuations in δD values for bulk organic matter have been identified in the Raton Basin, York Canyon site (Schimmelmann and DeNiro, 1984) which may indicate that fluctuations in the water balance or the temperature of the swampy freshwater environment at that time were minor when compared to other changes in the global setting (Meyers and Simoneit, 1990). Stable nitrogen isotope values indicate minor fluctuations but do not display any major long-term shifts (Schimmelmann and DeNiro, 1984).

One study, conducted on K/T boundary sediments from Stevns Klint, Denmark, reported the presence of two exotic amino acids, α-aminoisobutyric acid (α-Aiba) and isovaline (I-val) (Zhao and Bada, 1989). The distribution and stereochemistry of other amino acids in Stevns

Klint sediments have not been reported. There are currently two hypotheses for the occurrence of α-Aiba and I-val in Stevns Klint sediments. One is that they are extraterrestrial in origin (Zhao and Bada, 1989) and the other is that they are the by-products of the thermal alteration of coal (Olson, 1992). Another report, by Mita and Shimoyama (1998), suggests that industrial waste, when hydrolyzed, could produce both α-Aiba and I-val. The levels they found in Tokyo Bay were consequential, when compared with the other protein amino acids found in the bay sediments. The I-val was nearly racemic, suggestive of a non-biological source. There exist numerous other observations in the literature on the production, uptake, metabolism and effects of these exotic amino acids in bacterial, fungal, floral and faunal systems (e.g. Vogels and van der Drift, 1976; Griffith, 1986; Elliott and Watkinson, 1989). These latter trace biotic sources and effects are likely negligible in the settings in the present study.

An extraterrestrial origin for α-Aiba and I-val is based on the hypothesis that a collision occurred between a large bolide and the Earth (Zhao and Bada, 1989). Zhao and Bada (1989) suggested that the impact of a huge extraterrestrial body (approximately 10 km in diameter; Wetherill and Shoemaker, 1982) with the Earth would produce a distinct organic overprint, similar to the chemical composition of carbonaceous meteorites, such as the Murchison meteorite. Several organic compounds that are rare or non-existent on Earth, e.g. α-Aiba and I-val, have been identified in high abundance in the Murchison meteorite (e.g. Engel and Nagy, 1982).

Zahnle and Grinspoon (1990) have suggested that the amino acids were deposited from comet dust produced from either a massive comet trapped in the inner solar system or dust blown into the atmosphere from an impact, instead of directly from the bolide impact itself. Their reasoning for this is that the intense heat from an impact would destroy the amino acids. This might explain why Zhao and Bada (1989) did not detect α-Aiba and I-val in the boundary clay, but only above and below the boundary.

The second hypothesis is that α-Aiba and I-val were by-products of the thermal alteration of coal, i.e. coal gasification (Olson, 1992). Coal gasification produces large amounts of amino acid precursors, called hydantoins. The primary hydantoins are 5,5-dimethylhydantoin and 5-ethyl-5-methylhydantoin. Upon hydrolysis, these hydantoins yield α-Aiba and I-val, respectively (Olson, 1992). The high temperatures needed to promote natural coal gasification could be obtained by magma intrusions into coal beds, thus producing the hydantoins. This hypothesis would explain why α-Aiba and I-val are found centimeters above and below the K/T boundary and not at the boundary. However, it does not account for the Ir anomaly present at the boundary (Olson, 1992).

The objective of this study was to examine sediments at several K/T boundary sites to determine the overall distribution, stereochemistry and stable isotope composition of amino acids. The sites chosen for this study are the terreginous sediments of the Starkville South and Raton Pass locales in the Raton Basin of Colorado and New Mexico and the marine sediments of Stevns Klint, Denmark. This study establishes a baseline for comparison with the amino acids in other K/T boundary sediments, other terrestrial sediments and the Murchison meteorite. The working hypothesis in this study was that if any amino acids in the K/T boundary sediments are extraterrestrial in origin, then the amino acids should be enriched in ^{13}C relative to terrestrial organic material. This hypothesis is based on work conducted by Engel et al. (1990) on the Murchison meteorite where it was determined that α-Aiba and I-val had $\delta^{13}C$ values of $+5‰$ and $+17‰$, respectively. These values are significantly enriched in ^{13}C compared to amino acids in terrestrial materials Engel et al., (1994).

2. Geologic setting

2.1. Stevns Klint, Denmark

Stevns Klint is only one of several locations in Denmark where the K/T boundary has been stud-

ied (Fig. 1A). Stevns Klint is a 12 km long, 20–21 in high sea cliff, situated approximately 40 km south of Copenhagen, Denmark on the east coast of the Stevns Peninsula (Surlyk, 1979). This location shows well-defined exposures of the K/T boundary sediments (Ekdale and Bromley, 1984) and overlies a "fault-limited structural high between the eastern end of the Ringkobing-Fyn High and the Fennoscandian Border Zone" (Surlyk, 1979).

The late Maastrichtian (Cretaceous) period in Denmark is characterized by shallow marine carbonate deposits that are primarily pelagic in nature (Ekdale and Bromley, 1984). These deposits show little evidence of lateral or downslope transportation, such as turbidites. However, small-scale slumping may have occurred in the vicinity (Ekdale and Bromley, 1984). The area has a high concentration of burrows and bryozoans within the chalk deposited during this period (Surlyk, 1979). The top of the Maastrichtian chalk and the bottom of the Danian (Tertiary) Cerithium Limestone, based on biostratigraphy, appear to show a hiatus, or period of non-deposition (Ekdale and Bromley, 1984).

Between the Late Maastrichtian chalk and the Cerithium Limestone lies the Mg-smectite-rich Fish Clay (Elliott et al., 1989), a dark thin clay or marl layer, which contains the Cretaceous/Tertiary boundary (Christensen et al., 1973; Hsu, 1988). The southern most point of Stevns Klint contains the thickest section (20 cm) of the Fish Clay studied. Other locations, however, may contain somewhat thicker sections (Christensen et al., 1973). The deepest portions of the basins have the thickest units of Fish Clay and the unit subsequently thins towards the basin margins (Christensen et al., 1973). Christensen et al. (1973) subdivided this interval, Upper Maastrichtian through the bottom of the Cerithium Limestone, into six beds. The Upper Cretaceous white chalk (Bed I) contains burrows and scattered fossils. Above the chalk is a 1–2 cm. thick gray marl unit (Bed II) which is layered and thins out laterally. Bed III is a 1–2 cm, black marl bed containing small pyrite concretions. Bed IV is a light gray to black, laminated marl that is 3–5 cm. thick. A sharp transition leads to Bed V, a light gray marl that contains streaks and veins and reaches up to 7 cm in thickness. This bed gradually grades into the Cerithium limestone (Bed VI). The Cerithium limestone is white to light yellow in color, approximately 50 cm thick and is extensively bioturbated.

It has been suggested that Bed III was deposited under anoxic conditions based on the presence of pyrite and carbonate, the black color and organic carbon content of 1.2% (Ekdale and Bromley, 1984). Based on sedimentation rates, the anoxic conditions lasted less than 10 000 years
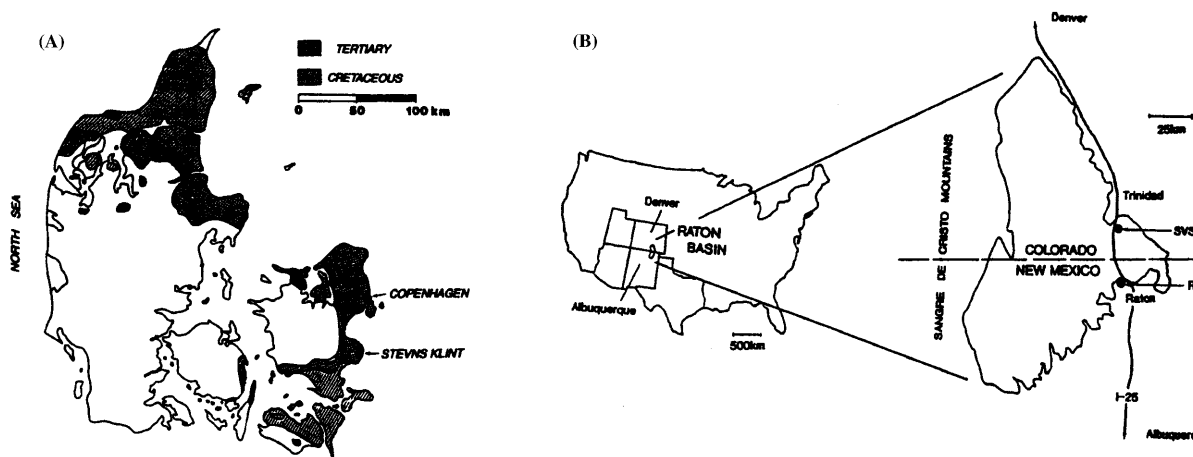

Fig. 1. Location of K/T sections in this study. (A) Stevns Klint, Denmark. (B) Raton Basin, United States.

and then returned to normal, pelagic sedimentation less than 300 000 years after the K/T extinction event (Hsu, 1988).

2.2. Raton Basin

The Raton Basin (Fig. 1B) is a Laramide structural and sedimentary basin located in southeastern Colorado and northeastern New Mexico (Johnson and Wood, 1956; Baltz, 1965). The basin is bounded by the Sangre de Cristo Mountains on the west, the Wet Mountains and Apishap Arch in the north and the Sierra Grande Arch to the east (Johnson and Wood, 1956; Baltz, 1965). The southern portion of the basin merges with the Las Vegas sub-basin (Johnson and Wood, 1956; Baltz, 1965). The basin is asymmetric in structure and contains an area of approximately 6250 km^2 (Pillmore and Flores, 1984).

During the Late Cretaceous, the Raton Basin was covered by an epeiric sea (Pillmore and Flores, 1984, 1987) and experienced extensive orogenic events that continued episodically through the Oligocene (Baltz, 1965). The first of these orogenic events, at the end of the Late Cretaceous, caused an epierogenic uplift west of the basin that may have formed mountains (Johnson and Wood, 1956). Erosion of the mountains produced coarse sands and gravels that were transported and deposited in the terrigenous environment of the Raton Basin region (Johnson and Wood, 1956). As the epeiric sea regressed to the east across Colorado and New Mexico during the late Campanian and early Maastrichtian (Cretaceous), non-marine sediments continued to be deposited until Paleocene times (Johnson and Wood, 1956; Pillmore and Flores, 1984).

The Raton Formation, containing the K/T boundary, was sourced from the mountains to the west as minor orogenic events occurred, causing erosion of the mountains (Johnson and Wood, 1956; Pillmore and Flores, 1984, 1987). Coarse material was transported from the source and deposited on an upper alluvial fan forming a conglomeritic sandstone (Pillmore and Flores, 1984, 1987). As the area stabilized tectonically, fine-grained sand, mud, silt and carbonaceous material were deposited on flood plains and swamps (Johnson and Wood, 1956; Pillmore and Flores, 1984, 1987).

The Raton Formation is subdivided into three zones: the lower coal zone, the barren series and the upper coal zone (Pillmore and Flores, 1984, 1987; Nichols, 1990). The lower coal zone contains the Cretaceous portion of the Raton Formation, with the K/T boundary lying at or near the top of this zone (Pillmore and Flores, 1987). The lower coal zone ranges in thickness from 30 m, east of the city of Raton, New Mexico, to 90 m in thickeness, west of Vermejo Park, New Mexico. Above the basal conglomeritic sandstone is a series of meandering-stream and interchannel deposits composed of medium to coarse-grained sandstone with interbedded lenses of conglomerate, which are quite thick in the western portion of the basin. Siltstone, mudstone, and sandstone beds interbedded with carbonaceous shale and thin coal beds comprise the remainder of the lower coal zone (Pillmore and Flores, 1987). The barren series is composed primarily of fine to coarse-grained channel sandstones containing en echelon cross-bedding. These sandstones are locally interbedded with and laterally grade into mudstone, siltstone and swamp deposits of coal and carbonaceous shale from floodplain deposits. The thickness of this zone ranges from 180 m in the west to 55 m along the eastern margin of the basin (Pillmore and Flores, 1987). The upper coal zone is composed of crevasse-splay very fine-grained sandstones, mudstones, siltstones and shales interbedded with carbonaceous shales and thick beds (1–2 m) of coal. The thickness of the upper coal zone ranges from 335 m in the central part of the basin to 180 m near the eastern edge (Pillmore and Flores, 1987).

The K/T boundary is found in various sites throughout the basin and in each instance the boundary is associated with a swamp environment. However, according to Nichols (1990), in each location there are sufficient differences to suggest that the boundary is independent of lithology. The boundary is identified in the Raton Basin based on the abrupt disappearance of vari-
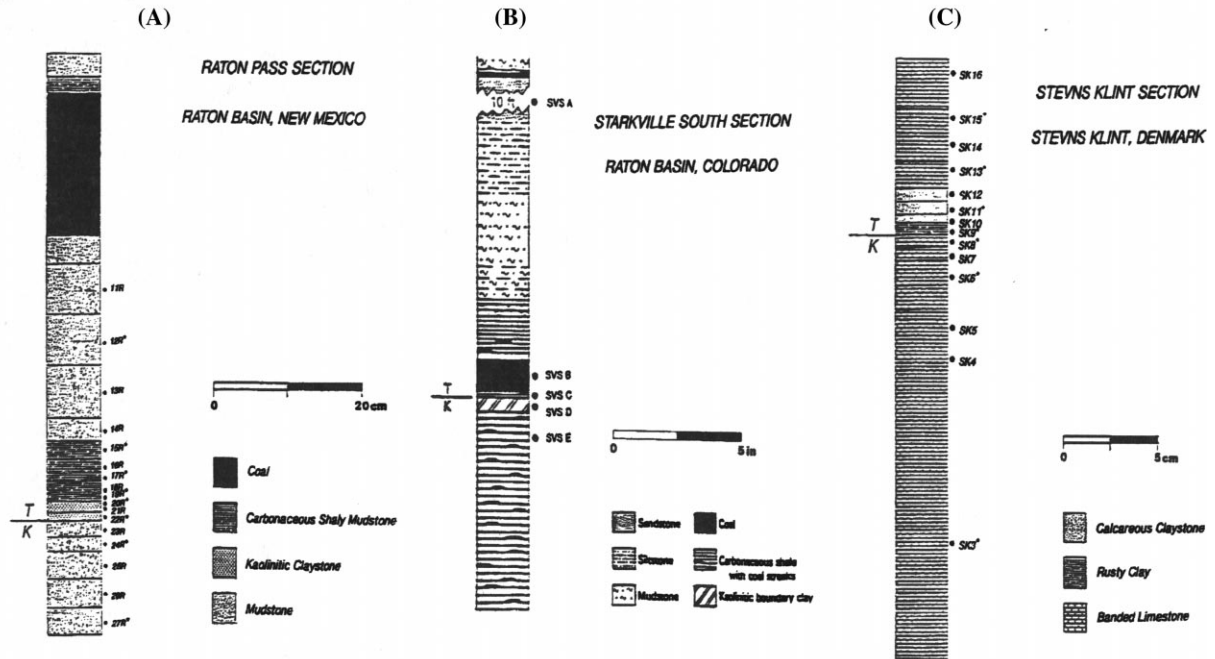
Fig. 2. Sample locations within each section. (A). Raton Pass, New Mexico. (B) Starkville South, Colorado. (C) Stevns Klint, Denmark.

ous taxa of fossil pollen, in particular, *Proteacidites*, *Tilia wodehousei sensu Anderson*, *Trisectoris*, and *Trichopeltinites* (Tschudy, 1970). The extinction of *Proteacidites* is simultaneous with the top of a 1–2.5 cm. thick clay bed termed the boundary clay (Pillmore and Flores, 1987). The boundary is composed of virtually pure, well-crystallized kaolinite with lesser amounts of other clays, has a fine grained texture, hackly to conchoidal fracture patterns and weathers to a light 'bone' color (Pillmore and Flores, 1987). This description of the boundary resembles that of numerous tonstein beds found in the Western Interior. However, the chemical compositions of the boundary clays differ from that of the average Raton tonstein beds (Williamson, 1970; Bohor and Pillmore, 1976; Pillmore and Flores, 1984, 1987). The boundary clay contains concentrations of Ir, titanium, scandium, vanadium, chromium and antimony that are increased by factors of four or more over their concentrations in all other Raton Basin tonsteins that were analyzed by Gilmore et al. (1984).

3. Methods

3.1. Sample acquisition

Two sites from Raton Basin, Colorado and New Mexico and one site from Stevns Klint, Denmark were sampled. The first of the Raton Basin sample locations is the Raton Pass site, located approximately 1.5 km west of the town of Raton, New Mexico, along the east side of the old Raton Pass road (Pillmore and Flores, 1987; Hildebrand, 1992). Dr Alan Hildebrand (Canadian Geological Survey) provided seventeen samples from this site, eight of which were examined in detail for amino acid abundances and stereochemistry. Two of the samples are from the boundary (20R is from the fireball layer and 22R is from the ejecta layer), four carbonate mudstone and shale samples (12R, 15R, 17R and 19R) lie above the boundary and two mudstones (24R and 27R) lie below the boundary (Fig. 2A).

The second of the Raton Basin sites is Starkville South, which is located 4.2 km south of

the Starkville, Colorado exit road (Pillmore and Flores, 1987). Dr Dale Russell (North Carolina State University) provided five samples from the Starkville South site. A boundary sample (SVS D) was collected along with two coals (SVS A and SVS B) and carbonate shales above (SVS C) and below (SVS E) the boundary (Fig. 2B)

The Stevns Klint, Denmark sample set consisted of sixteen samples collected by Dr. Alan Hildebrand, seven of which were analyzed for amino acid abundances and stereochemistry. A boundary sample (SK 9) was collected along with two limestones (SK 15 and SK 13) and one calcareous claystone (SK 11) above the boundary and three limestones (SK 8, SK 6 and SK 3) below the boundary (Fig. 2C). The samples from all three locations were powdered and homogenized prior to shipment to our laboratory.

3.1.1. Sample preparation

Each sediment sample was analyzed for total organic carbon and nitrogen as well as stable isotope compositions as described below. Next, the samples were analyzed for amino acid abundances, stereochemistry and stable carbon isotope compositions of the amino acids. Approximately 0.5–2.0 g quantities of the homogenized sediment samples were weighed and transferred to Pyrex test tubes and hydrolyzed with 14.0 ml of 6 M Ultrex HCl (Fisher Scientific). Stevns Klint samples were acidified with 6 M Ultrex HCl, to dissolve the carbonate, and then rotoevaporated and transferred to Pyrex tubes prior to the addition of 14 ml 6 M HCl The test tubes were shaken, flushed with N_2, sealed with Teflon-lined caps and heated for 24 h at 100°C. After hydrolysis, the samples were cooled and stored at 4°C until processing. The samples were filtered using 0.45 μ Gelman DM-450 membrane filters and rinsed with three aliquots of distilled water. The filtrates were concentrated by rotoevaporation and then desalted on a freshly regenerated 30 or 50 ml column of Biorad AG50-X8 (50–100 mesh, hydrogen form) cation-exchange resin. The amino acids were recovered using two bed volumes of 1.5 M NH_4OH and the samples were then concentrated by rotoevaporation until only 2–3 ml of solution remained. The samples were next filtered

through a Gelman Sciences Acrodisc (0.2 μ) or they were passed through a Whatman extraction column (C18/100 mg) into 4 ml vials and evaporated to dryness under N_2. Amino acid concentrations, stereochemistry, and stable carbon isotope compositions of the amino acid enantiomers were determined using high performance liquid chromatography (HPLC), gas chromatography (GC), and gas chromatography/combustion/isotope ratio mass spectrometry (GC/C/IRMS), respectively, as described below.

3.2. Analytical methods

3.2.1. High performance liquid chromatography (HPLC)

The dried amino acid extracts were dissolved in 0.01 M HCl and amino acid distributions were determined and quantified by HPLC using a cation-exchange resin column (15 cm × 2.3 mm, i.d., St. John Assoc., Beltsville, MD). The HPLC system was equipped with a four step-gradient sodium citrate buffer program (pH 3.25, 3.75, 4.25 and 10.0, respectively) that was delivered consecutively at time intervals of 10, 7, 18 and 40 min and at a flow rate of 0.08 ml/min. Amino acids were observed by post-column derivatization, with *o*-phthaldialdehyde and fluorescence detection. Replicate analyses of each sample were performed and a standard amino acid mixture was analyzed after each sample analysis. The amino acid concentrations were determined by comparing peak areas between the amino acids of the sample and those of the corresponding standard. The average error for amino acid concentrations was between 5 and 10%.

3.2.1.1. Gas chromatography. Aliquots of the desalted acid hydrolyzates were derivatized and analyzed by GC using a slightly modified procedure previously reported by Serban et al. (1988). Each of the amino acid samples was evaporated under N_2 at 40°C until dry, and then esterified with 0.3 ml of acidified isopropanol and heated at 110°C for 1 h. The samples were then cooled in the freezer for 5–10 min. Next, the samples were removed from the freezer and evaporated under a gentle stream of N_2 at 25°C until dry. The sam-

ples were acylated with 0.2 ml CH_2Cl_2 and 0.2 ml trifluoroacetic anhydride (TFAA) for 10 min at 110°C . The samples were chilled in the freezer for 5–10 min after the heating step and then evaporated under a gentle stream of N_2 at 25°C until dry (approximately 5–10 min). The sample derivatives were redissolved in approximately 0.1 ml CH_2Cl_2 and evaporated again to remove remaining traces of TFAA and trifluoroacetic acid. The samples were then dissolved in 0.2 ml CH_2Cl_2 for injection onto the GC.

Replicate GC analyses of each sample were performed on a Hewlett-Packard 5890 GC equipped with a 50 m × 0.25 mm i.d., fused silica column coated with an optically active stationary phase (Chirasil-Val III, Alltech Assoc., Deerfield, IL) for analysis of amino acid stereochemistry. Details of this GC method have been previously reported (Engel and Hare, 1985; Serban et al., 1988). Respective peak areas were used to calculate the amino acid D/L values.

3.2.1.2. Conventional isotope ratio mass spectrometry. Analyses for stable carbon and nitrogen isotopes for each bulk acidified (to remove carbonate) sediment sample. Each sample was loaded into a quartz tube (15 cm × 7 mm i.d.). Approximately 5 g of ashed copper oxide wire and 1 g of high purity native copper wire (Alpha Resources Inc.) were added, then the tubes were evacuated and sealed. The Dumas combustion method was used to convert the samples to CO_2 and N_2 and the resultant gases were purified cryogenically and analyzed for stable isotope compositions on a Micromass PRISM mass spectrometer as previously reported (Macko et al., 1987). Organic C and N contents of the samples were determined by manometric analyses of the CO_2 gas and from the ion intensities of the N_2 gas in a calibrated volume of the mass spectrometer, respectively. The stable isotopic ratio is reported as follows:

$$\delta^N E = [R_{sample}/R_{standard} - 1]10^3 (‰)$$

where N is the heavy isotope of the element E and R is the abundance ratio of the heavy to light isotopes ($^{13}C/^{12}C$ or $^{15}N/^{14}N$) of that element. The standard for carbon is the Peedee Belemnite lime-stone (PDB) and for nitrogen the standard is atmospheric N_2 (Air) which are assigned $\delta^N E$ values of 0.0‰. The reproducibility of the measurement is typically better than $\pm 0.2‰$. In the laboratory, the samples are commonly measured against tanks of carbon dioxide and nitrogen gases which have been calibrated against NBS 22 and atmospheric N_2, respectively.

3.2.1.3. Gas chromatography/combustion/isotope ratio mass spectrometry. Stable carbon isotopic compositions of individual amino acid enantiomer derivatives of the SVS samples were determined using a Micromass PRISM GC/C/IRMS system. The system consists of a Hewlett-Packard 5890 GC interfaced with a combustion furnace/water trap to the PRISM isotope ratio mass spectrometer (GC/C/IRMS). The amino acid derivatives and GC column conditions were identical to those described above for the GC analyses of the amino acid enantiomers. The CO_2 gas evolved during on-line combustion of the individual trifluoroacetyl isopropyl esters of the amino acids eluted from the GC column was, after removal of water, introduced directly into the mass spectrometer ion source. This instrument configuration permits stable carbon isotope analyses to be performed at nanomole levels (Silfer et al., 1991). The derivative $\delta^{13}C$ values were corrected to obtain the underivatized $\delta^{13}C$ values of the amino acid enantiomers using the procedure of Silfer et al. (1994).

4. Results

4.1. Amino acid distribution

4.1.1. Raton Basin

Total amino acid concentrations and organic N and C (%N, %C) contents for the Starkville South site (SVS) and the Raton Pass site (R) are listed in Table 1. At SVS, the boundary sample (SVS D) has a very low total amino acid concentration (26.2 nmol/g) whereas the other samples contain significantly higher concentrations, ranging from 127.9 nmol/g in SVS E to 499.1 nmol/g in SVS B. The two coal samples, SVS A and SVS B, con-

tained significantly higher total amino acid concentrations than the other sediments, i.e., 311.2 and 499.1 nmol/g, respectively. Total amino acid concentrations were lower overall in the Raton section samples. At Raton, the concentrations ranged from 32.0 nmol/g in 12R to 192.3 nmol/g in 17R. Amino acid abundances decrease above and below sample 17R. The boundary samples, 20R and 22R, which are below 17R, contain lower amino acid abundances than 17R. The common protein amino acids are the primary constituents of the Starkville South and Raton Pass sample sets (Table 2). Minor amounts of β-alanine, ornithine and γ-aminobutyric acid are also present. Based on retention time and the coinjection of an authentic standard, it is possible that α-Aiba is present in three of the Starkville South samples, SVS A, SVS B and SVS C, but not in the other two samples SVS D and SVS E. The overall distribution of amino acids in sample sets SVS and R is similar, with the neutral protein amino acids dominating the acidic and basic amino acids. Aspartic acid concentrations are consistently low in all samples, with the exception of the two coal samples (SVS A and SVS B) in the Starkville South site and 19R in the Raton Pass section. The possible presence of α-Aiba was detected only in the previously mentioned coal samples and the sample right below the coal samples, SVS C. Threonine and serine, thermally labile amino acids, are present throughout these two sample sets.

4.1.2. Stevns Klint

Total amino acid concentrations and organic C and N compositions for the Stevns Klint section are shown in Table 1. This marine sample set is quite distinct from that of the non-marine Raton Basin sections. The total amino acid concentration is considerably higher in the boundary sample (SK9, 530.7 nmol/g) than the surrounding samples. The samples above and below the boundary at Stevns Klint continually decrease in concentration with increasing distance from the boundary sample. This may be due to the paucity of organic material in the limestones above and below the boundary clay,

Table 1
Bulk carbon and nitrogen content of samples from K/T sections

	Amino acid concentration (nmol/g)	%C	%N	C/N
Starkville South				
SVS A	311.2	68.60	3.00	26.7
SVS B	499.1	63.90	2.40	31.7
SVS C	215.2	5.60	1.00	6.7
SVS D	26.2	0.30	0.10	5.0
SVS E	127.9	3.90	0.60	7.1
Raton Basin				
12R	32.0	0.42	0.03	11.7
15R	66.9	0.60	0.04	18.3
17R	192.3	1.55	0.14	13.0
19R	147.0	1.25	0.10	14.6
20R	74.0	1.32	0.09	17.6
22R	54.1	0.17	0.02	10.1
24R	53.4	0.47	0.02	32.2
27R	48.4	0.66	0.05	16.3
Stevns Klint				
SK3	135.7	1.30	0.10	15.2
SK6	138.0	1.76	0.11	18.6
SK8	224.0	3.12	0.15	24.2
SK9	530.7	2.67	0.24	12.9
SK11	400.0	2.64	0.23	13.4
SK13	169.4	1.96	0.11	20.7
SK15	132.3	2.00	0.16	14.6

Table 2
Amino acid concentrations (nmol/g) of individual samples from K/T sections

Amino Acid								
Starkville South	SVS A	SVS B	SVS C	SVS D	SVS E			
Asp	25.3	35.0	9.6	0.3	1.8			
Thr	20.2	32.7	13.1	1.9	6.9			
Ser	20.8	29.7	15.1	2.8	7.3			
Glu	27.8	43.2	20.9	1.4	7.0			
Gly	57.2	84.7	24.9	4.9	17.8			
Ala	51.2	89.0	55.7	5.4	25.8			
α-Aiba	1.0	3.9	0.4	–	–			
Val	21.6	36.2	17.2	2.2	25.8			
Met	1.4	4.2	1.1	–	1.1			
Ile	7.9	11.0	7.0	1.0	4.3			
Leu	21.5	40.3	14.7	1.8	8.8			
β-Ala	11.8	18.6	6.9	0.6	3.2			
γ-Aba	8.2	15.0	3.0	0.5	4.1			
His	24.6	38.1	23.9	3.2	13.3			
Orn	1.1	0.9	–	–	–			
Lys	8.4	9.8	1.8	0.4	0.7			
Arg	1.0	4.9	–	–	–			
Raton Basin	12R	15R	17R	19R	20R	22R	24R	27R
Asp	0.1	2.3	2.2	12.0	0.6	0.9	4.9	3.7
Thr	2.2	5.2	16.4	9.2	6.0	3.9	3.9	3.5
Ser	2.8	5.4	14.9	10.4	5.1	4.3	5.2	3.5
Glu	1.5	7.1	11.8	20.6	5.0	3.4	7.3	5.7
Gly	7.1	13.7	40.2	25.2	11.2	11.5	9.3	8.3
Ala	7.7	13.5	41.8	28.5	23.3	10.3	8.5	9.3
α-Aiba	–	–	–	–	–	–	–	–
Val	2.4	5.0	16.5	9.5	6.4	4.1	3.5	3.4
Met	0.5	0.5	1.2	3.4	0.4	1.1	–	0.2
Ile	1.3	2.7	8.8	4.3	2.7	2.2	1.9	1.9
Leu	2.7	4.9	15.8	9.1	4.9	3.9	3.4	3.3
Tyr	–	–	–	–	0.9	–	–	–
Phe	–	–	–	–	2.5	2.4	0.6	–
β-Ala	0.5	–	–	2.3	1.0	1.0	0.6	0.7
His	2.0	3.6	12.6	5.1	1.9	2.8	2.3	3.1
Orn	–	–	–	1.3	–	0.4	–	–
Lys	1.2	3.0	10.3	5.3	2.3	1.8	1.4	1.8
Arg	–	–	–	0.8	–	–	0.3	–
Stevns Klint	SK15	SK13	SK11	SK9	SK8	SK6	SK3	
Asp	9.8	14.1	50.4	59.4	24.3	17.6	18.2	
Thr	5.0	8.4	25.7	29.0	9.2	7.8	7.0	
Ser	5.8	7.2	24.0	24.6	13.3	7.8	7.8	
Glu	15.0	17.4	41.1	62.3	24.6	16.8	17.6	
Gly	25.9	31.6	69.3	79.5	35.1	23.8	24.6	
Ala	26.4	32.4	65.2	90.0	34.7	22.8	22.4	
α-Aiba	1.9	1.6	1.9	1.7	0.7	1.0	0.9	
Val	8.9	13.2	27.8	40.4	15.1	8.7	8.4	
Met	1.5	2.1	5.6	–	2.5	0.4	–	
Ile	4.2	7.7	19.1	26.1	9.4	4.8	4.6	
Leu	6.9	12.1	32.9	46.9	16.4	8.7	8.5	
Tyr	–	–	–	7.3	1.2	–	–	
Phe	–	–	–	13.5	2.0	–	–	
β-Ala	4.3	4.6	8.0	4.0	6.1	3.3	2.9	
γ-Aba	5.3	4.7	8.1	3.7	3.5	2.7	1.8	
His	7.0	6.9	21.1	21.2	13.5	6.1	4.7	
Orn	0.9	1.0	–	–	1.0	–	1.5	
Lys	3.0	3.9	–	21.2	9.1	4.6	4.2	
Arg	0.5	0.5	–	–	2.3	1.0	0.7	

which contains a higher concentration of organic material.

The amino acid distributions in the Stevns Klint samples differ from those of the Raton Basin. The individual amino acids are primarily the common protein amino acids, with minor contributions of β-alanine, γ-aminobutyric acid and ornithine. Acidic and neutral amino acids predominate the overall distribution of amino acids in these samples. Glycine and alanine are the most abundant of the individual amino acids (Table 2). The acidic amino acid (aspartic acid and glutamic acid) concentrations exhibit the same trend as the total amino acid concentrations, i.e., their concentrations are greatest at the boundary (SK9) and decrease with increasing distance from the boundary. The possible presence of α-Aiba was noted in all of the samples, with its concentration ranging from 0.7 nmol/g in SK8 to 1.9 nmol/g in SK15. Thermally labile amino acids, threonine and serine, were identified throughout the sample series. Their concentrations, however, are always lower than the acidic amino acids, aspartic acid and glutamic acid.

4.2. Amino acid stereochemistry

4.2.1. Raton Basin

A representative gas chromatogram for Starkville South (SVS B) is shown in Fig. 3. Five amino acids from the Starkville South samples and four from the Raton samples were adequately resolved to calculate the D/L values of the D- and L-enantiomers. The extent of amino acid racemization is low, in general below 0.37. The D/L values are variable within the sections and there are no obvious trends in the extent of racemization above or below the boundary samples.

4.2.2. Stevns Klint

The D- and L-enantiomers of five amino acids were adequately resolved for calculation of D/L values. The racemization levels are quite low in this sample set, ranging from 0.03 to 0.37, except for one anomalous value of 0.52 for alanine in sample SK15. The D/L values above and below the boundary (SK9), are slightly higher than the boundary values. Peak interferences in the gas
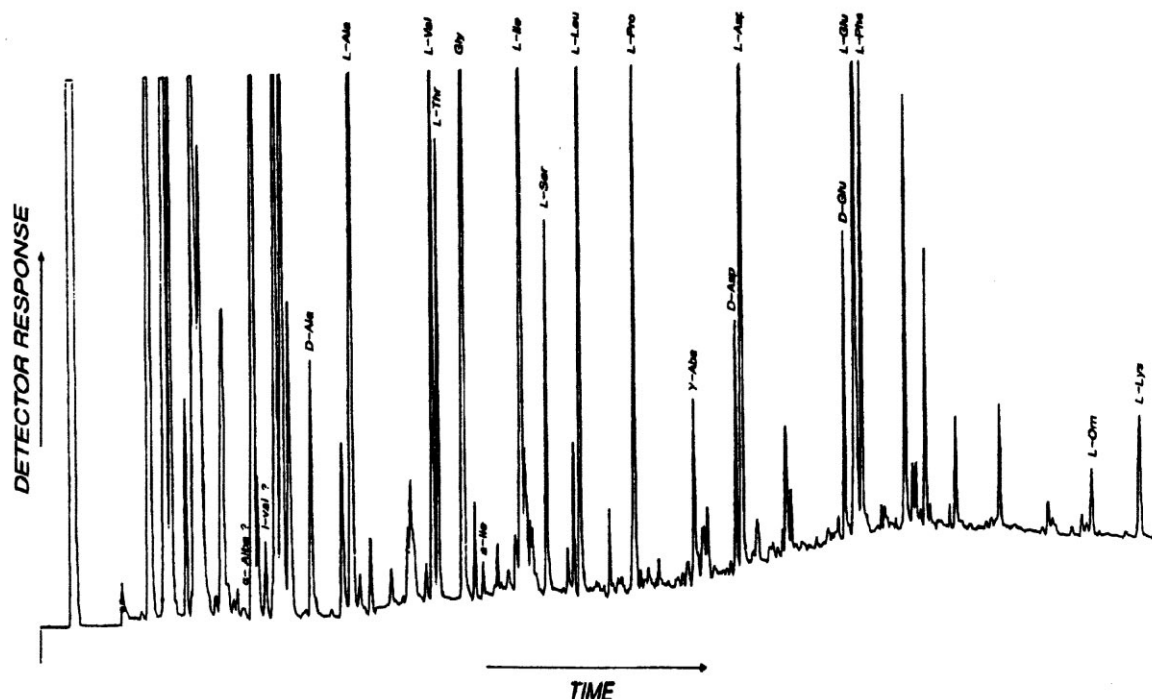

Fig. 3. Representative gas chromatographic separation of amino acid stereoisomers. Sample SVS B, StarkvilleSouth, Raton Basin.

Table 3
Bulk carbon and nitrogen stable isotope compositions (‰) of individual samples from K/T sections

	$\delta^{13}C$	$\delta^{15}C$
Starkville South		
SVS A	−25.8	+3.0
SVS B	−25.6	+3.3
SVS C	−27.9	+3.1
SVS D	−22.5	+0.8
SVS E	−25.0	+3.0
Raton Basin		
11R	−25.0	+3.3
12R	−24.9	+3.1
13R	−25.3	+2.6
14R	−25.8	+2.7
15R	−25.8	+3.2
16R	−26.5	+2.9
17R	−26.1	+3.2
18R	−26.5	+3.2
19R	−26.0	+4.3
20R	−26.1	+5.2
21R	−23.4	−0.1
22R	−25.5	+3.6
23R	−24.5	+3.3
24R	−24.5	+4.1
25R	−24.5	+4.5
26R	−25.1	+3.3
27R	−25.3	+3.4
Stevns Klint		
SK1	−25.9	+7.3
SK2	−25.8	+8.9
SK3	−25.9	+8.0
SK4	−25.9	+7.7
SK5	−25.3	+8.9
SK6	−25.5	+10.8
SK7	−25.4	+10.6
SK8	−25.5	+11.6
SK9	−25.5	+8.3
SK10	−26.0	+7.1
SK11	−25.8	+6.0
SK12	−25.7	+5.3
SK13	−25.4	+11.4
SK14	−25.6	+11.5
SK15	−25.4	+12.9
SK16	−25.3	+12.9

chromatograms for SK11 resulted in inadequate resolution to calculate D/L values for this sample.

4.3. Bulk stable isotopes

The $\delta^{13}C$ and $\delta^{15}N$ values for bulk organic matter in the Raton Basin and Stevns Klint sam-

ples are listed in Table 3. The $\delta^{13}C$ values for all three sections range from −25.0 to −27.9‰, the exceptions being the boundary samples in both Raton Basin sections, which are enriched in $\delta^{13}C$ by about 2‰. The $\delta^{15}N$ values for both Raton Basin sections ranged from +2.6 to +4.5‰, the exceptions once again being the boundary samples, which were depleted in ^{15}N by several per mil relative to adjacent samples above and below the boundary. The $\delta^{15}N$ values for Stevns Klint were enriched in ^{15}N relative to Raton Basin, ranging from +5.3 to +12.9‰. Unlike Raton Basin, there was no significant enrichment in ^{13}C or depletion in ^{15}N in the K/T boundary sample (SK9) at Stevns Klint.

4.4. Stable isotope compositions of amino acid enantiomers

Stable isotope analyses were conducted by GC/C/IRMS on the TFA isopropyl ester derivatives of amino acid enantiomers isolated from the Starkville South samples (Table 4). The derivative values were obtained and corrected to underivatized values for six amino acids. The $\delta^{13}C$ values ranged from −13 ± 1‰ for glycine to −31 ± 6‰ for L-isoleucine. All of the $\delta^{13}C$ values reported for the Starkville South section are extremely depleted in ^{13}C relative to those reported by Engel et al. (1990) for amino acid constituents of the Murchison meteorite (Table 4).

5. Discussion

5.1. Amino acid distribution

The amino acid distributions in the non-marine, Raton Basin sediments and the marine, Stevns Klint sediments both contained high concentrations of stable protein amino acids, e.g. glycine, alanine, valine and leucine. High concentrations of alanine may have resulted, in part, from the decomposition of other protein amino acids in the sediments (Serban et al., 1988). The concentrations of labile protein amino acids (e.g. threonine and serine) were about half that of the aforementioned amino acids, but are what would be ex-

pected if these compounds were entirely indigenous and of terrestrial origin. The fact that threonine and serine have been reported as only trace constituents of the Murchison meteorite (Engel et al., 1993) precludes the likelihood of an extraterrestrial origin for these compounds. Concentrations of aspartic acid and glutamic acid are considerably lower than observed in the Raton Basin section samples (excluding 19R and samples SVS A, SVS B, and SVS C) but this may reflect partial losses during the isolation of these compounds from the sediments.

Amino acid distributions at all three K/T boundary sections investigated do not reflect the amino acid distribution previously reported for the Murchison meteorite (Engel and Nagy, 1982). The Murchison meteorite contains high concentrations of several exotic, non-protein amino acids, including α-aminoisobutyric acid, isovaline, γ-aminoisobutyric acid and β-alanine, whereas the K/T boundary sediments contain only trace levels of some of these exotic constituents, and in samples other than the K/T boundary sections. It is more likely the presence of these amino acids is attributable to decomposition and microbial activity (Williams and Smith, 1977). The fact that the exotic amino acids are found at low levels in most samples above and below the boundary indicates, however, that a single source from an impact event, for these amino acids, is unlikely. Alternatively, Olson (1992) has proposed that exotic amino acids such as α-aminoisobutyric and isovaline in terrestrial sediments may have resulted from the hydrolysis of hydantoin precursors formed during high temperature thermal alteration of coals via contact with magmas or a bolide impact. The hydrolysis of hydantoins in industrial waste has been suggested to be the high (1 nmol/g) levels of α-aminoisobutyric and isovaline observed in Tokyo Bay by Mita and Shimoyama (1998).

The amino acid distributions for samples from the three localities studied are similar to those that have been reported for other modern sedimentary environments (Pulchan, 1987). Given the age of these sediments and their intermittent exposure to fluids over the millions of years following deposition, the acquisition and/or exchange of amino acids at various times seems likely (Macko and Engel, 1991).

5.2. Amino acid stereochemistry

Amino acids constituents of living organisms on Earth are comprised almost exclusively of the L-enantiomer (e.g. Engel et al., 1993). However, with the passage of time, L-amino acids undergo racemization and eventually approach racemic mixtures of the L-reactant and the D-product (Hare and Mitterer, 1966). Various environmental factors affect amino acid racemization rates, including temperature, pH, ionic strength and metal ions (Williams and Smith, 1977). Fossils of Miocene age, for example, have been reported to contain virtually racemic amino acids (Hare and Abelson, 1967). Studies, such as the one mentioned above, have led to the assumption that non-racemic amino acids found in fossils and sediments of Miocene or older age are most probably indicative of contamination owing to subse-

Table 4
Carbon isotope compositions (‰) of individual amino acids

		Raton Basin SVS D	SVS E	Murchison meteorite
Glycine	−12	−14	−12	+22
L-Alanine	−16	−16	−17	+27
L-Valine	−26	−27	−27	ND
Isovaline	ND[a]	ND	ND	+17
L-Leucine	−28	−27	−34	ND
L-Glutamic acid	ND	−18	−26	+6
α-Aminoisobutyric acid	ND	ND	ND	+5
L-Isoleucine	−27	−35	ND	ND

[a] ND = not determined.

quent exchange with the surrounding environment (Williams and Smith, 1977). It should be noted, however, that the diagenetic incorporation of amino acids into geomacromolecules may retard racemization (Rafalska et al., 1991), thus limiting the utility of stereochemistry as a criterion for assessing the absolute indigeneity of these compounds.

In general, the D/L values of amino acids in the K/T boundary sediments are extremely low (0.02–0.37), which is inconsistent with their age. Whereas three samples had slightly elevated D/L values (0.45–0.59), this may be attributed to a larger error resulting from the calculation of these values from very small peaks, as evidenced by the higher standard errors for replicate analyses of these samples. The presence of primarily non-racemic (predominately L-enantiomer) amino acids in the Raton Basin and Stevns Klint sediment samples suggests the introduction of contaminants from the surrounding environment subsequent to deposition. For example, aspartic acid D/L values for the K/T boundary sediments are similar to those reported by Rutter et al. (1980) for Quaternary age (greater than 53 000 years old) sediments containing wood fragments located at Bluefish Basin, Northern Yukon, Alaska.

5.3. Bulk stable isotopes

The trend in bulk $\delta^{13}C$ values for the Raton Basin sample sites (SVS and R) exhibit an enrichment in ^{13}C at the boundary (SVS D and 21R, respectively) compared to samples below and above the boundary (Table 3). A similar trend has been reported at several other K/T localities, including the Moreno Formation in California, Brazos River, Texas, several DSDP sites (Meyers and Simoneit, 1990; Meyers, 1992a,b) and Hor HaHar, Israel (Magaritz et al., 1985) where an enrichment in ^{13}C is observed at or just above the boundary. Schimmelmann and DeNiro (1984) reported an enrichment in ^{13}C at the K/T boundary and a depletion just above the K/T boundary located at York Canyon, Raton Basin which was similar to the ^{13}C compositions reported in the present study for the Starkville South and Raton locales.

Stable nitrogen isotope values for the boundary samples in both Raton Basin sections are depleted in ^{15}N by several per mil relative to samples above and below the boundary (Table 3). Schimmelmann and DeNiro (1984) also reported a depletion in ^{15}N at and just above the boundary at York Canyon, Raton Basin. The Starkville South samples decrease in %N with depth (Table 1), which may reflect absorption of organic materials or inorganic forms of nitrogen onto clay or other silicate surfaces (e.g. Degens and Mopper, 1976; Macko and Pereira, 1990).

Stable carbon isotope values for the Stevns Klint sample set showed very little change throughout the section. A slight depletion in the $\delta^{13}C$ values (0.5‰) was observed just above the boundary, which is similar to a ^{13}C depletion of 0.8‰ reported by Hansen et al. (1986) at the same location. The $\delta^{15}N$ values at Stevns Klint were depleted by about 3.3‰ at and just above the K/T boundary relative to samples below the boundary and further up section (Table 3).

Based on a similar enrichment in ^{13}C and depletion in ^{15}N, it is suggested that boundary samples SVS D and 21R are stratigraphically equivalent. The $\delta^{13}C$ isotope values may be clues to global wildfires. This is supported by studies of natural charcoals and atmospheric carbon particulate material from biomass fires that contain carbon isotopic compositions ($\delta^{13}C = -25.4‰ \pm 0.3‰$) similar to those found at the K/T boundary (Gilmour et al., 1989). Large amounts of soot reported from the Raton Basin and Stevns Klint locations has been attributed to global fires of biomass initiated by an impact (e.g. Tschudy et al., 1984; Wolbach et al., 1985). It is implied based on the $\delta^{13}C$ values that a single homogenized source from a global event was needed to produce such constant $\delta^{13}C$ values (Gilmour et al., 1989).

The depletion reported in $\delta^{15}N$ values from Raton Basin may be explained by the incorporation of atmospheric nitrogen (0.0‰) into the soils and plants. This incorporation may have been biologically (nitrogen fixation) or abiotically (high temperature oxidation) mediated. The $\delta^{15}N$ fluctuations in the Stevns Klint samples can best be explained by changes in productivity and/or lithology (Shemesh et al., 1993).

5.4. Stable carbon isotopes of individual amino acid enantiomers

The stable carbon isotope values reported for individual amino, acids from Starkville South were extremely depleted in ^{13}C relative to the δ^{13}C values reported by Engel et al. (1990) for the Murchison meteorite (Table 4). These results indicate that an extraterrestrial signal, if indeed present, is being totally overwhelmed by a terrestrial overprint. This would suggest that the δ^{13}C values from the K/T sediments are primarily composed of modern terrestrial material.

6. Conclusions

The amino acid distributions for the three K/T boundary locations studied appear to be similar to those reported for modern terrestrial materials. The exotic amino acids, α-aminoisobutyric acid and isovaline, are found at low levels in many of the samples studied, at locations above and below the boundary. This would indicate that a single source or event for these amino acids, is unlikely. The D/L values of amino acids in the K/T boundary sediments are low (0.02–0.37), which is inconsistent with their age. This may be due to the introduction of modern materials (i.e. contaminants) into the sediments at various times. Bulk δ^{13}C and δ^{15}N values at the Starkville South and Raton sites were enriched in ^{13}C and depleted in ^{15}N, possibly supporting the K/T boundary fireball scenario. Bulk δ^{15}N values at the Stevns Klint locale suggest that changes in the isotope values are due to changes in productivity and/or lithology. The stable carbon isotope values reported for individual amino acids from Starkville South were extremely depleted in ^{13}C relative to those reported for the Murchison meteorite, indicating that any extraterrestrial signal that may be present is being masked by a terrestrial overprint. At present it has not been possible to obtain δ^{13}C values for α-aminoisobutyric acid and isovaline owing to their low abundances and peak interferences. Future attempts at obtaining these values, as well as the δ^{15}N values of the amino acids (Macko et al. 1997; Engel and Macko, 1997), via

the processing of larger sediment samples and isolation of these components by preparative chromatography will be required to resolve the question of whether these amino acids are of an extraterrestrial origin or resulted from the thermal alteration of terrestrial organic matter.

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