GEOCHEMICAL CHARACTERIZATION OF HIGH MOLECULAR WEIGHT ORGANIC MATERIAL ISOLATED FROM LATE CRETACEOUS FOSSILS

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Abstract

This study reports the first carbon and nitrogen isotope and amino acid analyses of high molecular weight (HMW) organic material isolated from bones and teeth of reptiles from Late Cretaceous vertebrates (Judith River Formation, Alberta). These data assist in the evaluation of indigeneity of the HMW component and assessment of trophic structure among the Late Cretaceous consumers. Amino acid analysis of the HCl hydrolyzates of these samples show an abundance of glutamic acid and glycine. The apparent presence of hydroxyproline and hydroxylysine in some samples coupled with the high concentration of glycine suggests that a remnant of the original organic material has been retained.

Ratios of the D- to L- enantiomer of amino acids values are less than 0.25. This may result from incorporation of the amino acids into high molecular weight organic components. Differences in amino acid patterns and enantiomer ratios between the organic fraction from fossils and associated sediment argues against contamination.

Stable carbon and nitrogen isotope values of the vertebrates range between -27 and -23$^{o}/_{oo}$ and -1 and 12$^{o}/_{oo}$ respectively. The $\delta^{15}N$ of consumers increase with trophic level. Within the terrestrial and aquatic habitats, $\delta^{15}N$ among some of the more predominant vertebrates

increases in the order panoplosaur < hadrosaur < ceratopsid < tyrannosaur and Aspideretes < champsosaur < crocodile < plesiosaur, respectively. These isotope signatures and trends in nitrogen values are typical of large modern herbivores and carnivores and are consistent with previously held views of the ecology of these organisms. The amino acid and isotope data suggest that a biochemical signal may be maintained throughout diagenesis. Such a signal could provide exciting new information pertaining to the comparative biochemistry, metabolism and ecology of fossil assemblages.

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Table of Contents

List of Tables

List of Figures

1.0 INTRODUCTION

1.1 General Statement

Biogeochemists working on modern environments are faced with the problem of ordering the limited data gained in the field into a logical framework that describes the system. Those studying paleoenvironments are faced with the similar, and more challenging task, of unravelling paleoecological interrelationships involving organisms and their environments from only a small sample of past life. Geochemical approaches, such as the stable isotope tracing technique described in this study, can provide unique insight into various aspects of paleoecology that have been difficult to assess with more traditional methods.

Within a prehistoric context, assessment of various aspects of community ecology such as species diversity, abundance and biomass, faunal interactions, and habitat preference are constrained by differential preservation of fossils, incomplete sampling, and lack of direct observations. The ability to evaluate ecosystem processes, nutrient cycling and energy flow, for a paleoenvironment is most severely limited by the inability to obtain *in situ* measurements. Nevertheless, the study of ecosystem processes is fundamental to the understanding of factors that controlled community structure. The availability of energy and nutrients controls biomass of the population,

the numbers of individuals in the population, and species diversity whereas the path of transfer influences faunal interactions and habitat ranges.

Nutrient cycling and energy flow within paleoenvironments have been indirectly considered through attempts to identify feeding habits and define energetic relationships (Ostrom, 1964; Stokes, 1964; Ostrom, 1966; Waldman and Hopkins, 1970; Bakker, 1971; Coombs, 1971; Farlow, 1976; Beland and Russell, 1978; Rensberger et al., 1980). Paleodiets have been inferred through the study of skeletal and dental structure, comparisons of fossil to *modern organisms, and the analysis of fossilized stomach contents and coprolites. According to these analyses, consumers are classified into broad categories such as herbivore or carnivore, and smaller sub-categories such as browser, grazer or granivore. These broad trophic level classifications provide a very simple and generalized framework for understanding patterns of energy flow.

The primary source of error in studies of energetics is the use of values extrapolated from modern populations to evaluate parameters, such as standing crop, for a prehistoric community. In addition, assessment of energy flow is based on the relative abundance of predators and their prey. Specific pathways of energy transfer cannot be derived from the knowledge of the relative abundance of

predator and prey.

Although these traditional methods provide a framework for understanding trophic interactions, they lack the resolution required to understand complex relationships. Some of the more detailed information, such as specific feeding habits that link species in a food web, the base of support to the food web, and molecular pathways of nutrient cycling, are difficult to derive from the fossil record.

Alternatively, geochemical analyses of organic substances in fossils offer a unique opportunity to obtain information about organisms and their paleoenvironments. Recent advances include the delineation of phylogenetic relationships of Pleistocene fauna using immunological techniques, the use of DNA-DNA hybridization to define phylogenetic and evolutionary trends, and the evaluation of prehistoric diet and metabolism through stable carbon and nitrogen isotope ratios (Schoeninger et al., 1983; Bada, 1985; DeNiro, 1987; Tuross et al., 1988; Lowenstein, 1988; Marshall, 1988). Geochemical analysis of organic matter obtained from fossils can assist in defining relationships that can not be directly derived from the fossil record.

Stable isotope analysis can provide information pertaining to energy transfer and resource partitioning. This method is based on modern dietary reconstructions

that indicate a similarity between the $\delta^{13}C$ and $\delta^{15}N$ [1] of the muscle tissue of an organism and its diet and have identified a correlation between increasing trophic level and increasing $\delta^{15}N$ values (Fry and Sherr, 1984; Minigawa and Wada, 1984; Harrigan et al., 1989). Consequently, $\delta^{13}C$ and $\delta^{15}N$ can be used to identify dietary sources of carbon and nitrogen and $\delta^{15}N$ is also used as an indicator of trophic structure. In contrast to inferential assessments based on dental remains and the calculation of energetic parameters, carbon and nitrogen isotope ratios are a direct indicator of feeding relationships.

This study attempts to evaluate pathways of energy transfer among late Cretaceous vertebrates from the Judith River formation. Analyses of the $\delta^{13}C$ and $\delta^{15}N$ of a high molecular weight (HMW) organic material isolated from fossils of aquatic and terrestrial food webs are used to establish feeding relationships and to determine sources of C and N that provide nutritional support to consumers. As there are no definitive marine sediments within the Judith River Formation in the Park, analyses of marine individuals are limited to a mosasaur from the Bearpaw Formation,

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[1] Isotopic compositions are expressed as:
$$\delta^{N}E = [(R_{sample}/R_{standard}) - 1] \times 1000$$
where N is the heavy isotope of element E and R is the abundance ratio of the heavy to light isotope. The standard for carbon is the Chicago Peedee Belemnite (PDB) and for nitrogen is atmospheric N_2.

Alberta and a mosasaur and shark from the Niobrara Formation, Kansas. Information on amino acid abundances and enantiomers together with the isotope data assists in assessing the indigeneity of the HMW organic fraction.

1.2 The Judith River Formation Within Dinosaur National Park

1.2.1 Geological Environment

Dinosaur Provincial Park (DPP) in southeastern Alberta contains extensive badland exposures of the Judith River Formation (Figure 1). Within this locality, the entire formation is approximately 250m thick. The nearly flat-lying badland exposures within the park represent only the upper 90m of the formation (MacDonald et al., 1987). Although the Judith River Formation constitutes the majority of the exposures, an outcrop in the eastern section of the park exposes the basal 20m of the Bearpaw Formation (Eberth, in press). The Judith River-Bearpaw boundary represents a transformation from fluvial to marine facies (Koster, 1984). This sequence records the last major transgressive/regressive cycle of the Western Interior Seaway in North America.

The Judith River Formation is a channel-dominated coastal plain sequence dated at 74-76 Ma by radioisotope

dating (K-Ar and ^{40}Ar-^{39}Ar: Folinsbee et al., 1964, 1965; Steiger and Jaeger, 1978; Thomas et al., in press, Eberth et al., in press). Koster (1984) and Koster et al. (1987) believe that the paleochannels represent a varied estuarine environment ranging from high sinuosity to distal, low sinuosity reaches. Alternatively, Wood et al. (1988) present a fluvial, meandering-channel depositional model whereby the upper 60m of the Formation is interpreted as the product of channel floor, point bar and overbank sedimentation by high-sinuosity, freshwater rivers. Eberth (in press) interprets the formation as a coastal sequence in which low sinuosity rivers of ephemeral flow and no tidal influence are found in the lower 20m, meandering rivers subject to tidal backwater effects characterize the intermediate bed, and the uppermost exposures record a transgressive sequence shifting from coastal-plain through paralic facies of the Lethbridge Coal Zone. Presently, a consensus as to the relative validity of the two models does not exist.

1.2.2 Paleoenvironment

During the mid-Campanian, DPP constituted the distal part of a flat low-lying coastal plain (Dodson, 1971; Marsaglia and Klein, 1983). Floral, faunal, and sedimentary evidence indicate a humid, warm temperate to

subtropical environment (Dodson, 1971; Beland and Russell, 1978; Jarzen, 1982, Dodson and Gnidovec, 1982; Koster, 1987). The moist environment supported an abundant diverse flora with common occurrences of cypress, cycads, tree ferns, herbaceous lilies, and parasitic mistletoes (Jarzen, 1982).

This coastal flatland was strongly influenced by southeastward-flowing rivers (Koster et al., 1987). Stream beds 35 to 165 m in bankfull width and 5 to 25 m in depth could easily accommodate fauna enroute between estuarine and inland environments (Wood, 1985; Visser, J., 1986). Periods of high flood discharges produced ephemeral mud-laden flood waters in interchannel areas (Wood et al., 1988; Koster et al., 1987). Increased tidal influence and proximity to the sea may have occurred over the 2 million years that encompasses the exposed sequences of the Judith River Formation in DPP (Eberth, in press).

1.3 Vertebrate Assemblage

The dinosaur assemblage from the Judith River Formation in DPP is regarded as one of the most important in North America (Beland and Russell, 1978). This area is acclaimed for its extraordinarily high diversity and large number of relatively well-preserved skeletal fragments. Dinosaurs represent 35 of the 127 species of vertebrates

recorded from the park (Eberth, 1989). The eight most common vertebrates include four genera of hadrosaurids (Lambeosaurus, Corythosaurus, Kritosaurus, Prosaurolophus), two ceratopsids (Chasmosaurus, Centrosaurus), one ankylosaurid (Euoplocephalus), and one tyrannosaurid (Albertosaurus) (see Appendix 2 for taxonomy of the Late Cretaceous vertebrates discussed in this study). In addition to the dinosaurs, remains from 32 taxa of fish, 29 taxa of non-dinosaurian reptiles, 10 amphibians, 20 mammals, and one bird have been documented (Eberth in press).

Present knowledge of the paleoecology of the Judith River fauna is largely based on interpretations of functional morphology and the relative abundance of vertebrate remains with regard to location and taxa (Dodson, 1971; Beland and Russell, 1978; Brinkman, in press). With regard to food web structure, these studies offer very general information regarding habitat utilization, community structure, and feeding mechanisms. This dissertation uses stable isotopes to delineate food web structure. This approach is particularly useful for defining trophic position and sources of carbon and nitrogen supplied to the food web. The conceptual framework for the interpretation of these data, outlined below, draws upon information from previous paleoecological

interpretations and modern analogies.

For considerations of trophic interactions, Late Cretaceous vertebrates can be grouped into three categories: aquatic (fish, plesiosaurs, champsosaurids, crocodiles, dermatemydid and trionychid turtles), mesofauna (vertebrates estimated to be less than 100kg in size: baenid turtles, pachycephalosaurids, ornithomimids, small theropods) and terrestrial megafauna (tyrannosaurids, ankylosaurians, ceratopsids, and hadrosaurids; Beland and Russell, 1978). Terrestrial and aquatic paleocommunities have been segregated into inland and coastal components (Brinkman, in press). Some salient distinctions include the assignment of the crocodile Leidyosuchus, Champsosaurus, a trionychid turtle, and Myledaphus to the aquatic coastal community and ceratopsians to the coastal terrestrial community.

These divisions will be used in this dissertation to assist in assessment of food web relationships. In this regard, grouping according to habitat is useful because nutrient sources, foraging strategies and feeding relationships are dependent on ecosystem type and community structure. Furthermore, such a separation will assist in defining the type and the size of prey that is available, the mobility of predators, and the morphological adaptations for feeding that exist within a particular

ecosystem These attributes are primary determinants of dietary composition. The conception of faunal interactions within Late Cretaceous aquatic and terrestrial communities is described below. This information provides the framework for the discussion of trophic relationships later in this study.

1.3.1 Aquatic Community

Within the aquatic community consumers from both coastal and inland environments ultimately derive nutrition through either a planktonic or detrital-based food web (Hynes, 1970; Moss, 1980). Many different organic sources can contribute to each of these pools. Phytoplankton can be composed of groups such as blue-green algae, diatoms, and green algae. Detritus can be derived from fecal pellets, autochthonous benthic vegetation and allochthonous input from terrestrial environments. In addition, the species that constitute the phytoplankton and detritus will differ between coastal and inland waters. The following consideration of pathways of energy transfer among consumers are a basic model and, thus, distinctions between inland and coastal wetlands have not been made.

Nutrients from primary production are transferred to zooplankton and deposit feeders (e.g. crustaceans and insect larvae) through either grazing or filter feeding.

Many turtles, including the extant dermatemydid, Dermatemys mawei, are also herbivorous (Halliday and Adler, 1987). Other turtles, such as extant members of the Trionychidae, are omnivores. These animals feed on insects, crustaceans, and fish (Halliday and Adler, 1987).

The feeding habits of secondary consumers, such as fish, often vary markedly with size. Differences in feeding habits can occur during a life cycle and among individuals who differ in stature (Hynes, 1970; Moss, 1980) Whereas zooplankton often comprise the diet of small or young fish, larger individuals can be entirely piscivorous. The sharply pointed teeth of the plesiosaur and those of the champsosaur, a gavial-like reptile, suggest that fish contributed to the diet of these organisms (Estes, 1964; Norman, 1985; Russell, 1989).

Large secondary consumers may have foraged on numerous types of prey. Crocodiles may have been one of the most versatile predators during the Cretaceous (Russell, 1989). The diet of modern crocodilians ranges from large invertebrates to birds and mammals (Cott, 1961; Halliday and Adler, 1987).

1.3.2 Terrestrial Community

Ecosystems within the terrestrial environment ranged from bald cypress swamps and peat bogs at the edge of the

delta to inland flood plains and nearby forests. A variety of nutrient sources for herbivores was possible within this varied landscape. Basic tendencies in herbivory were strongly influenced by height of the vertebrate and dental apparatus. A profile indicating feeding height for the megaherbivores suggests that hadrosaurs, ceratopsians and nodosaurs, and ankylosaurs fed at 4m, 2m, and less than 1m, respectively (Coe et al., 1987). At a height of 4m hadrosaurs could chose among branches of megafloralspecies including conifers and cypress. Efficient grinding of woody plants was made possible by solid dental structures and continual tooth replacement (Ostrom, 1964). The fossilized stomach contents of one hadrosaur contained needles, twigs, and seeds from conifers (Krausel, 1922). This finding may indicate that the diet of this hadrosaur consisted of coarse plants.

The unusual beaks and lower foraging height of the ceratopsians suggest a food source that is different from that of the hadrosaurs. The adaptations for consumption of a unique plant source are discussed by Ostrom (1966). The combination of the hooked beak and slicing teeth that form vertical shearing blades may have been used for tearing fronds of cycads, cycadeoid bennettites, or palms. Alternatively, fruits may have served as a food source for these dinosaurs (Berry, 1924; Krassilov, 1981).

Ankylosaurs, such as the nodosaur and panoplosaur discussed in this study, foraged on low plants (Beland and Russell, 1978). The broad toothless beak and the small posterior teeth of these organisms were more suited for cropping than chewing (Coe et al., 1987). It has been suggested that Euplocephalus was particularly adapted for foraging on the herbaceous layer (Beland and Russell, 1978).

In addition to these herbivorous megafauna, the mesofauna also included primary consumers such as Stegoceras. Few suggestions have been made regarding the specific diet of this pachycephalosaurid. However, the cuspate, serrated teeth could have been used to shred plants (Norman, 1985).

Nutrients from primary producers are transferred through these herbivores to omnivorous and carnivorous vertebrates. Ornithomimids were toothless and, thus, have been suggested to eat eggs, fruit, and small mammals (Russell, 1989). The apex of the trophic hierarchy was completed by the small bipedal carnivorous theropods such as Campsognathus (not analyzed in this study) and Coelophysis (not analyzed in this study), dromaeosaurids, and larger tyrannosaurids.

1.4 Taphonomy

Three modes of fossil preservation have been identified within DPP. These include articulated skeletons, bone beds, and isolated single bones. The majority of articulated skeletons are associated with trough cross-bedded sandstones interpreted as channel floor and lower point-bar deposits (Koster et al., 1987; Wood et al., 1988). It is thought that, prior to substantial disarticulation, carcasses were introduced into channels by cut bank collapse or overbank entrainment, transported downstream and interred by large-amplitude dunes (Wood et al., 1988). Preservation of trough cross-bed sets of up to 1.2m emphasizes the magnitude and burial potential of the aggrading dunes (Wood et al., 1988).

Bonebeds are thin concentrations of disarticulated, abraded skeletal remains (Koster et al., 1987; Wood et al., 1988). High diversity beds are interpreted as channel-base lag deposits entering the rivers by surficial sheet-flow, run-off or cut-bank collapse. Measurements of trough set thickness in one location average 0.7m. In addition to fossils, these deposits contain mudstone intraclasts, rare extrabasinal pebbles, small cobbles, and reworked siderite concretions in a fine-grained sandstone matrix (Koster et al., 1987; Wood et al., 1988).

Low diversity bonebeds are associated with point bar

deposits. (Wood et al., 1988). High concentrations of remains typically lie within intraformational conglomerates of mudstone pebbles in a fine-grained sandstone. The Centrosaurus bonebed with an average of 20 element$\cdot m^{-2}$ may contain the remains of approximately 300 individuals. The monogeneric tendency of these large assemblages suggest mass mortality of a herd of animals prior to transport downstream and stranding on point bars (Koster et al., 1987; Wood et al., 1988).

A third grouping of vertebrate fossils, microfossil sites, consists of a diverse assemblage of small fossils dominated by teeth, fish scales, dermal bone and vertebrae elements (Rodson, 1971; Wood et al, 1988; Brinkman, in press). Such fossil groupings occur in channel and overbank facies (Eberth, in press). In-channel accumulations were locally derived during bank collapse and rip-up events. Those in overbank facies primarily form during the process of flooding and aggradation associated with crevasse splay deposits (Eberth, in press).

Isolated single bones most commonly occur in channel-fill sequences (Koster et al., 1987). In this case, disarticulation long preceded bedload transport, deposition, and burial by aggrading dunes. Preservation ranges from unabraided to broken bone.

Among these taphonomic modes, fossilization within

channels through rapid transport and burial is a common process. High faunal densities in combination with these circumstances resulted in a system that was conducive to preservation (Dodson et al., 1980; Beland and Russell, 1978; Koster, 1987; Behrensmeyer, 1988).

1.5 Niobrara Chalk

During the Late Cretaceous the area extending from Kansas to southern Manitoba was a shallow, clear, calm sea, with nearly anoxic bottom waters (Miller, 1968; Russell, 1989). An outstanding degree of productivity of coccoliths resulted in an accumulation of calcium carbonate. Within this environment, faunal remains slowly developed an encasing matrix of calcite particles (Matter and Miller, 1972). Subsequent compaction and lithification of these sediments and fossils resulted in the 200m thick chalk beds of the Niobrara Formation.

1.6 Carbon and Nitrogen Isotope Analysis

1.6.1 Theory

Biogeochemical studies involving the use of stable carbon and nitrogen isotopes as tracers make use of very small variations in the natural abundances of carbon and nitrogen isotopes that occur in the reservoirs of these elements. The isotopic composition of a sample is expressed

as, approximately, a parts per thousand difference from a standard:

$$\delta^{N}E = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) X\ 10^{3}$$

where N is the heavy isotope of element E, carbon or nitrogen, and R is the ratio of the trace to abundant isotope. The international standard for carbon is Peedee Belemnite (PDB) limestone and for nitrogen it is atmospheric nitrogen, N_2.

Variations in the isotopic composition of different sources of carbon and nitrogen can be a result of fractionation, i.e. discrimination between isotopes due to either equilibrium or kinetic effects. Equilibrium effects occur during exchange reactions, are temperature dependent and are mechanism independent. The isotopic composition of the molecules involved in equilibrium reactions can be correlated to their energy state as seen in vibrational spectra. Unlike equilibrium reactions, kinetic effects occur during reactions that involve an activated complex and are both temperature and mechanism dependent. Variations in isotopic composition in biological systems are due to kinetic effects (Macko and Engel, in press for discussion and examples of isotope effects). These result from differences in the rates at which the heavy and light species react.

1.6.2 Modern Food Web Analysis

Stable carbon isotopes have been used to trace carbon flow from plant sources to consumers in a variety of terrestrial, aquatic (fresh water), and marine food webs (Minson et al., 1975; DeNiro and Epstein, 1978; Teeri and Schoeller, 1979; Thayer et al., 1978; Fry and Parker, 1979; Harrigan et al., 1989). These laboratory and field studies found that the whole body or muscle tissue of animals frequently reflect dietary values within 1 to 2‰. This slight variation between the organism and its diet is due to fractionation that occurs during the formation and breakage of bonds during biosynthesis (Abelson and Hoering, 1961; Winters, 1971). Several investigations also showed that the magnitude of the difference between the $\delta^{13}C$ of an individual and its diet was dependent on tissue type (DeNiro and Epstein, 1978; Tieszen et al., 1983; Harrigan, et al., 1989).

Stable carbon isotopes provide a useful tracer within natural populations when trophic level shifts are accounted for. Their use is best illustrated for herbivores consuming either C_3 or C_4 plants, that differ by more than 10‰ in $\delta^{13}C$ (Minson et al. 1975; Fry and Parker, 1978). Carbon isotope values can also be used to differentiate marine from terrestrial food webs, to distinguish between

various estuarine communities, and to identify populations of a single species feeding within isotopically distinct locations (Fry, 1981; Rodelli et al., 1984; Zieman et al., 1984; Schoeninger and DeNiro, 1984; Harrigan et al., 1989). These and other food web studies have been fairly successful in demonstrating the relative importance of various primary producers in the diet of animals (Fry, 1977; Thayer et al., 1978; Fry and Parker, 1979). However, precise feeding relationships cannot be defined when the sources of dietary carbon are isotopically similar. It is possible that food sources, indistinguishable by $\delta^{13}C$ may be separated with $\delta^{15}N$.

Like carbon, the nitrogen isotopic composition of a consumer and its diet are comparable and most similar when based on the analysis of the whole organism (Miyake and Wada, 1967; Wada et al., 1975; DeNiro and Epstein, 1981; Tieszen et al., 1983; Harrigan et al., 1989). The $\delta^{15}N$ of an organism shows a consistent $+3^{o}/_{oo}$ enrichment relative to its food source (Miyake and Wada, 1967; Wada, 1979; DeNiro and Epstein, 1981; Macko, 1981; Macko et al., 1982; Harrigan et al., 1989). This enrichment, that occurs with each trophic level along the food chain, provides a measure of energy flow and a basis for establishing trophic structure (Fry, 1986; Harrigan et al., 1989; Dickson, 1987).

Several food web studies have combined the use of carbon and nitrogen isotope tracers (Fry, 1981; Schoeninger and DeNiro, 1984; Zieman et al, 1984; Harrigan et al., 1989; Dickson, 1987). In these cases $\delta^{15}N$ values were most valuable in differentiating among ultimate food sources that could not be separated based on carbon isotope values alone (e.g., macroalgae versus seagrass, offshore versus estuarine particulate organic matter, and algae versus mangrove) and in evaluating trophic structure. Dual isotope tracers provide mutually supporting data for distinction between terrestrial and marine food sources and provide necessary information for making quantitative estimates of ultimate dietary sources of carbon and nitrogen to complex food webs (Miyake and Wada, 1967; Sweeney and Kaplan, 1980; Harrigan et al., 1989).

In addition to whole samples, isotopic analysis can be extended to individual amino acids. The resulting amino acid labeling pattern provides another food web tracer. Winters (1971) was the first to isolate individual amino acids from animals for $\delta^{13}C$ analysis. Subsequent studies have shown that amino acids from bones of animals fed a controlled diet have a carbon and nitrogen isotope pattern that could be related to the specific food source (Hare et al., 1986; Hare et al., in press).

1.6.3 Prehistoric Dietary Reconstructions

Numerous archeological studies have used the stable isotope analysis of collagen from fossil bones for reconstructing the diet of prehistoric human populations (Chisholm et al., 1982, Schoeninger and DeNiro, 1982; Hobson and Collier, 1984; Ambrose and DeNiro, 1986). Only a few attempts have been made to distinguish feeding relationships among nonhuman fossil organisms (Nelson et al., 1986; Katzberg, 1989). The archeological data demonstrate, just as in modern food webs, that carbon isotope ratios can be used to differentiate between prehistoric consumption of C_3 and C_4 plants (van der Merwe, 1982; Schwarcz et al., 1985). Both $\delta^{13}C$ and $\delta^{15}N$ values distinguish between utilization of marine and terrestrial food sources (Tauber, 1981; Chisholm et al., 1982, 1983; Schoeninger et al, 1983; Schoeninger and DeNiro, 1984). Consumers of dominantly marine-based diets show $\delta^{13}C$ and $\delta^{15}N$ values that are enriched by approximately $+7^{o}/_{oo}$ and $+9^{o}/_{oo}$, respectively, relative to terrestrial C_3 consumers (Figure 2). Isotopic variation among consumers within an ecosystem is, in part, a function of trophic shifts and variation in the signature among primary producers (Ostrom and Fry, submitted).

These studies described above do not illustrate a detailed food web analysis. A more complete

characterization requires comparisons of consumers and food sources collected from the same area. If more detailed or supporting data is required, molecular level isotope mapping offers an additional source of paleodiet information. Applications of this new approach have been limited to two studies (Tuross et al., 1988; Hare et al., in press). The nonessential amino acids of bones from a fossil bison (10,000 - 11,000 y.b.p.) and a prehistoric whale (70,000 years old) were isotopically similar to collagen from modern analogs. This retention of the pattern of the amino acid signatures suggests that prehistoric diets may be assessed through a comparison of fossil and modern collagen.

1.7 Indigeneity of Organic Material Isolated From Fossils

An accurate interpretation of feeding habits of prehistoric organisms based on geochemical analysis depends on the ability to isolate a remnant of the original material. An evaluation of indigeneity is presently based on an assessment of the distribution and relative abundance of amino acids, carbon to nitrogen elemental ratios, a comparison of the isotopic composition of the fossil material to that of a modern analog, and knowledge of the extent to which individual amino acids have undergone

racemization (Armstrong et al., 1983; Hassan and Hare, 1978; DeNiro, 1985, Tuross et al., 1988; Serban et al., 1988).

Evidence of an indigenous signal from organic material isolated from fossil bones and teeth has been based on geochemical comparisons to modern collagen (Hare, 1980; Armstrong et al., 1983; Schoeninger et al., 1983; DeNiro,985). The amino acid composition of the modern protein is characterized by high glycine (Gly) and proline (Pro) content, approximately 35% and 12%, respectively, and the presence of hydroxyproline (Hypro) and hydroxylysine (Hylys, Lehninger, 1979; Hare, 1980). Although the yield of organic matter from fossils is lower than it is from modern bones and teeth, high concentrations of Gly and the presence of Hypro and Hylys have been observed in Pleistocene to Recent fossil materials by several workers (Wycoff, 1972; Tuross et al., 1978; Nelson et al., 1986). In many cases, it has been shown that isotopic signatures also appear to be retained (Schoeninger et al., 1983; Nelson et al., 1986; Tuross et al., 1988).

The process of amino acid racemization has been reviewed by Schroeder and Bada (1976). Owing to postmortem effects, the existence of a non-racemic mixture in fossils that are more than 2 million years old could be construed as evidence of alteration or contamination (Hare and

Mitterer, 1966). However, a preponderance of the L-enantiomer may exist if the amino acid isolated for analysis originated from a higher molecular weight proteinaceous fraction or a non-proteinaceous component such as humic-like material (Weiner et al., 1976; Hoering, 1980; Kimber and Griffin, 1987). The amino acids of HMW material from the Late Cretaceous fossils in this thesis are expected to be non-racemic.

Ratios of elemental carbon to nitrogen have also been used as an indicator of diagenesis (DeNiro, 1985; Nelson et al., 1986). Extensive alteration of organic matter isolated from fossils was indicated by C/N values that diverged from the normal range for modern bone collagen (2.9 to 3.6). Such shifts in C/N were associated with deviations of more than $5°/_{oo}$ in $\delta^{13}C$ and $\delta^{15}N$ of fossil material relative to the isotopic composition of modern counterparts. Values of C/N within the range of modern collagen are consistent with what would be expected from an indigenous collagenous component.

The inability to detect collagen in a fossil does not unequivocally indicate contamination. Noncollagenous proteins have been successfully identified by immunological techniques in fossil bone material (Tuross, 1987). As a consequence of postmortem degradation of the protein matrix, the probability of isolating a material that is

similar to the original collagen decreases with increasing age of the fossil (Wyckoff, 1972; Hare, 1980; Tuross et al., 1988). Interpretation of data from older specimens requires knowledge of the geochemical characteristics of the organic fraction that remains after long term diagenesis. Geochemical characteristics fossil materials may not be entirely consistent with those observed for modern collagen.

High molecular weight intracrystaline material with a strong affinity for the hydroxyapatite mineral phase is thought to be the organic component that is most resistant to diagenetic processes (Weiner and Price, 1986; Curry, 1988, DeNiro and Weiner, 1988). Using synthetic hydroxyapatite as a stationary phase, chromatographic studies have shown that proteins and peptides containing carboxylic acid groups are specifically absorbed to this mineral (Bernardi and Kawasaki, 1968; Moreno et al., 1984). Consequently, high concentrations of the dicarboxylic amino acids (aspartic acid and glutamic acid) obtained from a high molecular weight fraction may be characteristic of a remnant of the original organic material. Such amino acid patterns are typical of noncollagenous proteins but could also result from selective binding of a collagen degradation product (Linde et al., 1984; Masters, 1987).

1.8 Techniques for Isolating Organic Matter From Fossils

Previous studies have used mechanical cleaning, centrifugation techniques and dialysis to assist in the removal of contaminants (Wycoff, 1972; Weiner et al., 1979; Armstrong et al., 1983; DeNiro and Weiner, 1983; Serban et al., 1987). Mechanical cleaning method assist in the removal of surface contaminants but do not effectively remove low molecular weight contaminants which can easily migrate into fossils and be retained within matrix. Methods that include a centrifugation technique provide for the removal of materials that are extracted by acid or base and retained in the supernatant subsequent to dialysis. The mechanical cleaning and dialysis technique used in this study provides for the removal of surface contaminants and low molecular weight material. A similar procedure used by Serban et al. (1987) and Weiner (1979) has been successful at isolating well-preserved material from fossil shells.

1.9 Study Objectives

This study reports the first attempt to evaluate food web structure of Late Cretaceous vertebrates using stable isotope analysis of a HMW organic material isolated from the fossil by a dialysis procedure. Fossils of terrestrial,

marine, and aquatic vertebrates were obtained such that a comparison could be made within, as well as among food webs associated with distinct environments. Fossils from a marine environment include samples of a mosasaur from the Bearpaw Formation, Alberta and of a mosasaur and shark from the Niobrara Formation, Kansas.

With the exception of samples from a size series of hadrosaur femora, non-porous fossils or portions of fossils were chosen to reduce the potential of contamination. Selectivity for non-porous samples and mechanical cleaning was not possible for the hadrosaur femora series as these samples were obtained in powdered form. Consequently, the degree of contamination prior to dialysis could not be determined. The presence of contaminants could result in differences in the geochemical characteristic between HMW material isolated from samples of the hadrosaur femora size series and HMW material prepared from whole bones or teeth of hadrosaurs. A comparison of the isotopic and amino acid composition between a porous and non-porous section of a single ceratopsid bone is made to assess the effects of porosity on the geochemical signal of the fossil.

The use of stable isotopes as dietary tracers requires isolation of an indigenous component that retains the geochemical signatures of the living organism. As

evidence of indigeneity, the HMW material of the fossils is characterized in terms of distribution and abundance of amino acids, enantiomer ratios, and stable carbon and nitrogen isotope values. This fraction is compared to an aliquot of the predialysate or total organic fraction (TOF) to evaluate the effects of the isolation technique. In an attempt to assess contamination, data from the TOF and HMW component from the fossils are compared to the TOF and HMW organic fraction obtained from the associated sediment. These comparisons assist in demonstrating the indigeneity of the HMW organic material and the validity of the isotope approach. Statements of the hypotheses to be explored in this study are listed below and, for clarity, will be cross referenced in the discussion of the results and conclusions. As indicated after the statement of each hypothesis, the findings of this study will be directed at characterizing the HMW material, assessing its indigeneity or assessing the effects of the isolation procedure.

Yield of HMW Material

1. The yield of HMW material from fossils is expected to be less than the yield of collagen obtained from modern bones and teeth. Results will assist in characterization.

C/N Values

1. If a collagenous component is present, the C/N of HMW material from fossils is expected to be within the range of values reported for modern collagen (2.9-3.6). Results will assist in characterization and may assist in determining indigeneity.
2. The samples that could not be mechanically cleaned (samples of the hadrosaur femora size series) are expected to differ from samples which were well cleaned. Results assist in determining the effects of mechanical cleaning.

Enantiomer Ratios (D/L Values)

1. The HMW material isolated from fossils is expected to be non-racemic. The results from this test assist in characterization and indigeneity.
2. The D/L of amino acids of HMW material from fossils is expected to be different from the D/L of the amino acids from the TOF of the fossils. The TOF contains low molecular weight material which were are excluded from the HMW material and, presumably, could be a source of contamination. The results of this test assist in characterization and/or evaluating indigeneity.
3. The D/L of the amino acids from HMW material of

fossils is expected to be different from D/L of the amino acids from the TOF and HMW material from sediments. The distinction in D/L values would be related to differences in racemization rates and origin of organic material. The results will assist in evaluating indigeneity.

Amino Acid Abundances

1. The yield of amino acids from HMW material of fossils is expected to be less than that of collagen from modern bones and teeth but similar to the yield of amino acids previously reported for Cretaceous fossils from various localities. Organic materials are lost from bones and teeth during diagenesis. The results will assist in characterization of the HMW material.
2. The amino acid distribution of HMW material from fossils is expected to retain some of the characteristics of modern collagen and NCP. This would be indicated by high concentrations of Gly and the presence of Hyp and Hyl. The results will assist in characterization and evaluating indigeneity.
3. The amino acid composition of the TOF and HMW material from fossils is expected to differ.

Differences in amino acid patterns would be related to lack of low molecular weight material in the HMW fraction. Assuming that the low molecular weight material is, in part, a contaminant, the results will assist in evaluating indigeneity.

4. The following pairs are expected to differ in their amino acid composition and yield:
   A. LMW material of sediment and HMW material of fossils
   B. HMW material of sediment and HMW material of fossils
   C. HMW material from porous bone and HMW material from non-porous bone

   Results from the above comparisons assist in establishing indigeneity.

Materials from the sediment and those that could not be removed from the porous fossil are sources of contamination to ancient bones and teeth. The geochemical characteristics of a fossil which did not have these contaminants should differ from that of the organic component of non-porous vertebrate remains and sediments

Stable Isotope Data

1. The $\delta^{13}C$ and $\delta^{15}N$ of HMW material from fossils are expected to be comparable to the isotopic

composition of modern analogs. Results assist in characterization and evaluating indigeneity.

2. Nitrogen isotope values of consumers are expected to be good indicators of trophic level. Results assist in evaluating indigeneity.
3. The following pairs are expected to differ in $\delta^{13}C$ and $\delta^{15}N$:
    A. HMW material of hadrosaurs bones received in a powdered form and HMW material of whole bones or teeth.
    B. HMW material of fossils and TOF of fossils.
    C. HMW material of fossils and HMW material of sediments.
    D. HMW material of fossils and TOF of sediments.

    The above comparisons assist in evaluating indigeneity.

2.0 METHODS

2.1 Acquisition of Samples

Fossil animals from the Judith River Formation in Dinosaur Provincial Park, the Bearpaw Formation, and the Niobrara Formation were obtained from established collections of National Museum of Natural Sciences, Ottawa, Ontario (courtesy of D.A. Russell) and Tyrrell Museum of Palaeontology, Drumheller, Alberta (courtesy of D. Brinkman, Table 1, Figure 1). These specimens were originally obtained from the upper 90m of the exposed portion of the Formation. Specific sampling localities for the entire sample set are only known for fossils obtained from microsites. The suite of specimens includes taxa from marine, aquatic, and terrestrial habitats, and are thought to span a range of trophic levels. A size series of hadrosaur femora is also included in the sample set (Table 2). Fossils from this series were ground to a powder by a different laboratory. Consequently, the extent of mechanical cleaning could not be determined for these samples.

Two samples of fossil plants from the Bearpaw Formation were obtained from David Eberth, Tyrrell Museum of Palaeontology, Drumheller, Alberta. Despite the younger age, the taxa are representative of vegetation occurring during the Judith River time (Table 3). Primary criterion

for selection was the high degree of preservation among these floral remains.

Sediment samples were obtained from five different locations that correspond to microsites from which fossil material was obtained (Table 1, Figure 1). One sediment sample was obtained directly from the surface of a tyrannosaur bone (Table 3).

2.2 Purification of High Molecular Weight Organic Matter

Purification of high molecular weight organics from fossil specimens and modern materials followed a dialysis procedure similar to that of Weiner et al. (1979). Prior to the isolation of the HMW organic material, skeletal remains were carefully cleaned in an ultrasonic bath of distilled water. This was followed by abrasion with an electric hand drill and acid etching (1.0N HCl). Microscopic examination assisted in the verification of contaminant removal. Hadrosaur femora within the size series were obtained in a powdered form and could not be subjected to this extensive precleaning. Samples of sediment from which HMW material was isolated were not pretreated prior to the dialysis procedure described below.

The cleaned vertebrate material and sediments were ground to a fine powder and dissolved in cold 6N HCl. The

resulting solution was dialyzed (Spectrapor 6, 6000-8000 MW cut off) at low temperature (2° to 5°C) against distilled water to eliminate the low molecular weight organic and mineral components. The HMW material retained by dialysis was freeze-dried prior to analysis. With the exception of the series of hadrosaur femora, the amount of freeze-dried HMW material was between 0.8 and 8.8 percent of the weight of the predialysate powder. The wide range in yield of HMW material from fossils is thought to result from varying contributions from an HCl insoluble inorganic mineral phase.

Collagen from a beef bone was also extracted by the same dialysis procedure. The modern material was cleaned of muscle tissue, freeze dried, ground to a fine powder, and dissolved in cold 6N HCl. The resulting solution was dialyzed using the same procedures that were described for the fossils. The weight of the freeze-dried material that resulted from a sample of 12.0 g was 1.3 g.

2.3 Preparation of Flora and Sediments

Owing to the limited amount of material, the floral material was not subjected to mechanical cleaning or the dialysis procedure. The floral remains were etched with 10% HCl, ground to a fine powder and acidified with double distilled 10% HCl to remove carbonate prior to isotope

analysis.

Sediments were ground to a fine powder. One aliquot of this material was used for isolation of HMW material (described above) and a second was used for geochemical analysis of the total organic component. There is no pretreatment of sediment for the analysis of total organic matter, with the exception of acidification (30% HCl) to remove carbonate prior to isotope analysis.

2.4 Stable Isotope and Elemental Abundance Determinations For Carbon and Nitrogen

Conversion of the organic nitrogen and carbon in the HMW material (10 to 25 mg), collagen (5.0 mg) or fossil plant (20 mg) to gases of suitable purity for stable isotope analysis was accomplished by a Dumas combustion in a sealed quartz tube (Macko, 1981). Precombusted copper oxide, pure copper and sample were added in the ratio of 5:1:1 to the samples in an ashed quartz tube. Evacuated samples were combusted to 850°C for one hour and allowed to cool gradually to prevent the formation of carbon monoxide and nitrous oxides.

Carbon dioxide and nitrogen gas were separated cryogenically from the combustion products on a vacuum line. The purified gases were analyzed for their $\delta^{13}C$ and $\delta^{15}N$ compositions on a VG Prism mass spectrometer. All

samples were analyzed by comparison to laboratory gas standards that were previously calibrated with respect to NBS standards. Isotope ratios are reported in per mil notation relative to PDB and atmospheric nitrogen for carbon and nitrogen, respectively. Precision for $\delta^{13}C$ and $\delta^{15}N$ is $\pm 0.1^{o}/_{oo}$. The reproducibility of $\delta^{13}C$ and $\delta^{15}N$ analyses (average difference between duplicate measurements) of dialyzed samples was $\pm 0.3^{o}/_{oo}$.

Abundance measurements for nitrogen gas samples were determined using a calibrated volume within the mass spectrometer. The ion beam produced is proportional to the pressure of the gas. Carbon abundance was determined on a calibrated manometer during cryogenic gas separation.

2.5 Determination of Amino Acid Abundances

An aliquot of the HMW material from fossils or modern teeth and bones (6 to 10 mg), sediment (200 to 300 mg), or HMW material isolated from sediments (100 to 200 mg) were hydrolyzed with quartz distilled 6N HCl for 24 h at 100° C and analyzed by ion exchange chromatography for the abundance of amino acids (Hare, 1977). After hydrolysis an aliquot (50 to 200μL of fossil HMW material) was dried under a stream of filtered air and brought up to 400μL in twice quartz distilled water. High molecular weight material from modern skeletal parts did not require this

concentration step. For such materials, a 50μL aliquot was diluted to 5mL. A 100μL volume of the resulting solution was injected onto a high performance liquid chromatograph (HPLC) column containing cation exchange resin (5μm particle size) for amino acid separation. A stepwise isocratic elution was achieved using buffers of constant ionic strength (pH 3.0, 3.25, and 10.1) introduced sequentially. Isolated amino acids react with ortho-phthalaldehyde reagent (OPA), to produce fluorescent derivatives that have intensities proportional to the concentration of the amino acid (Hare, 1972).

2.6 Determination of Amino Acid Enantiomers

The abundance of amino acid enantiomers was determined by gas chromatography (HP5790A or HP5840) with a flame ionization detector (FID) or mass selective detector (MSD). Ion fragmentation patterns were determined by analysis of individual amino acids using a scanning mode (50 to 500 mass to charge (m/z), 1.7 cycles per second). This provided the necessary information for a single ion monitoring program used with the MSD and a mass spectral library for tentative identification of sample components (Appendix 2). A mixture of 13 amino acid D- and L- pairs was used as a standard.

The amino acids within the mixture (hydrolyzate of the

sample or the standard) were converted to volatile forms for gas chromatography through a derivatization procedure. As described below, this involved esterification of the amino acids with acidified (-N) isopropyl alcohol followed by acylation of the ester with triflouroacetic acid anhydride (TFAA) or pentaflouropropionic anhydride (PFPA). Analysis and preparation of N(O,S)-TFAA-isopropyl esters was carried out by J.A. Silfer, Department of Geology and Geophysics, University of Oklahoma. Prior to derivatization with TFAA, samples were dried on a rotary evaporator, and desalted on Biorad AG 50W-X8 cation exchange resin (BioRad Laboratories). Amino acids were eluted from the column with 2M NH_4OH. The column eluant was evaporated to dryness and used for derivatization of N-TFAA-isopropyl esters. A desalting procedure was not used prior to derivatization with PFPA.

References for derivatization steps can be found in Engel and Hare (1985). The isopropyl alcohol for esterification was acidified by addition of acetyl chloride (one part acetyl chloride and four parts isopropyl alcohol) or by introducing HCl as a gas into the alcohol (0.16 g HCL 1.0 g $CH_3CHOHCH_3^{-1}$) to yield 3.5 N HCl in alcohol. An aliquot of the hydrolyzate (50 to 150 μL) was placed in a precombusted Teflon vial and dried under a stream of filtered air at room temperature. An excess of

acidified alcohol (100 μL) was added to the residue . The vials were sealed with Teflon caps and refluxed at 100° C for 45 minutes. After cooling, this mixture was evaporated to dryness under N_2 at 0° C and acylated with PFPA or TFAA (100 μL) at 100° C for 10 minutes. Samples were subsequently cooled and taken to dryness under a stream of N_2 at 0° C.

The resulting N(O,S)-TFAA-isopropyl or N(O,S)-PFP esters were redissolved in methylene chloride for separation on a Chirasil-Val (Applied Science) capillary column (25m X 0.25 mm I.D.). The optically active stationary phase is composed of N-propionyl-L-valine tert-butylamide coupled to a co-polymer of carboxyalkyl methysiloxene and dimethysiloxene. Samples were injected into the inlet of the gas chromatograph at a temperature of 215° C. The initial column temperature was 90° C and after 1.8 minutes the column was programmed to 200° C at a rate of 1.8° C min^{-1}. For elution of high boiling contaminants the column was held at 200° C for 10 minutes. The FID was set at 205° C and a single ion monitoring mode was used on the MSD for maximum sensitivity.

2.7 Statistical Treatment of Data

Many of the hypotheses listed in Section 1.9 are simple comparisons between two sample sets that require a

test for the difference between two means. When the sample size was three or greater, a t-test was used with a criterion for significance of α=0.01. When the sample size was less than two, two observations seperated by 4σ were determined to be significantly different. The standard deviation, σ, used in this case represents the standard deviation of replicate analyses.

3.0 RESULTS AND DISCUSSION

The primary objective of this dissertation is to use stable carbon and nitrogen isotopes to assess food web structure among Late Cretaceous vertebrates. This requires the isolation of a remnant of the original organic component from the fossils and the verification that the isolate retains an isotopic signal that is representative of the once living organism. The indigeneity of the HMW material isolated from the remains of Late Cretaceous vertebrates is assessed through an evaluation of C/N values, ratios of amino acid enantiomers, amino acid abundances, and isotope values of this material. In addition, comparisons among the HMW material and TOF from fossils and similar fractions obtained from the sediment assist in evaluating contamination.

3.1 High Molecular Weight Material: Yields and Carbon and Nitrogen Elemental Composition

The organic geochemical compositions of modern and fossil bones and teeth are related to the type of material that is analyzed. The yield and C/N of the HMW material isolated from fossils in this study will be compared to the yield and C/N of different organic fractions previously isolated from modern and fossil bones. These materials include collagenous and non-collagenous fractions as well

as an organic component retained in mineral aggregates (Miller and Wycoff, 1968; Hare, 1980; Nelson et al., 1986; Masters, 1987; DeNiro and Weiner, 1988). The yield and C/N varies among these fractions and between modern and prehistoric samples (Tables 4 and 5). Comparisons among different organic fractions from modern and fossil materials show that 1.) collagenous proteins are much more abundant than noncollagenous proteins (NCP) in modern materials, 2.) there can be a lower yield of collagenous material from fossils relative to modern materials, 3.) C/N do not appear to differ between modern and ancient collagenous and NCP fractions, and 4.) aggregates have an extremely wide range in C/N, with values greatly exceeding those for other fractions.

As a consequence of age and associated diagenesis, an indigenous organic component isolated from fossils analyzed in this study would only be a remnant of the original organic matter. Fossils of Late Cretaceous terrestrial and aquatic vertebrates, other than the hadrosaur femora, yield 0.2 to 9.6% HMW material (Tables 4 and 5). The average yield is 4.3% with a standard deviation of 2.4%. This variability and the large range of recovery is typical of that observed for collagenous and aggregate associated organic fractions obtained from Pleistocene fossils (Table 4, Nelson et al., 1986; DeNiro and Weiner, 1988). Although

not well-investigated, variations in the extent of diagenetic processes such as wetting and drying and composition of ground water may be associated with differences in the persistance of an organic matrix among prehistoric vertebrate remains. There may be differential effects of such processes among individual fossils within a single environment of deposition. Alternatively, the wide range in yield of the HMW material may be a consequence of varying contributions from an HCl insoluble inorganic mineral phase.

Excluding the hadrosaur femora size series, HMW materials from Late Cretaceous terrestrial and aquatic vertebrates have C/N values that vary from 1.5 to 16.6, with an average and standard deviation of 7.3 ± 4.2 (Tables 4 and 5). Samples of marine fossils also fall within this range (Table 5). Average percent carbon (%C) and percent nitrogen (%N) of the HMW material is 6.6 ± 6.4% and 1.5 ± 1.0, respectively. The differences in C/N among samples appear to be a function of the changes in %C. Both the HMW material and organic fraction associated with aggregates have C/N values that are variable and higher than collagenous and NCP fractions (Table 4). Such characteristics are typical of melanoidins and humic materials (Hoering, 1973; Schnitzer, 1985; Steelink, 1985).

The mechanism for the formation of humic acids is a reasonable model of a pathway of diagenesis by which organic matter may become preserved in fossil bones and teeth. This initial process involves the hydrolysis of organic compounds (i.e. biopolymers). Products resulting from this reaction (e.g. amino acids, sugars) are chemically reactive and may condense to form humic like materials over time.

Specifically, amino acids and sugars can react to form melanoidins (Maillard, 1913; Hoering, 1973). Sugars may originate from glycosylamines. These amino sugars have long been recognized as small yet significant components of the mineralized matrix of bones and teeth (Herring, 1968; Fisher et al., 1983; Veis, 1984). Localization of glycosylamines in the mineral matrix has also been confirmed (Fisher et al, 1983).

It is thought that the rearrangement of glycosylamine during intermediate stages of the Maillard reaction results in products that are not as readily metabolized as their precursors (Hoering, 1973). Through this mechanism, organic matter could be removed from the carbon cycle and preserved. Subsequent degradation of the rearrangement product results in compounds that further react with each other and with other starting materials to form resistant polymers. The above sequence of mechanisms is thought to

be one of several operative pathways for the formation of humic acids (Stevenson, 1974).

Polymeric material resulting from the condensation of amino acids and sugars could account for the high C/N of the HMW material obtained in this study. Variations in the carbon compositions of the starting materials as a consequence of differences in the degree of diagenetic effects prior to burial could also yield the observed wide range of C/N values. Alternatively, variation in the amount of carbon lost through dialysis could also affect C/N. Independence of the isotope signal from C/N suggests that C/N values can not be used as criteria for evaluating isotope data. For example, despite the large range for C/N of five hadrosaur samples, 1.5 to 13.0, the range in $\delta^{13}C$ and $\delta^{15}N$ values is less than 2.3 and 1.0°/$_{oo}$, respectively.

The yield of HMW material obtained from hadrosaur femora (average = 5.57 ± 3.44) is not significantly different from that obtained from other Late Cretaceous vertebrates (average = 4.25 ± 2.35, t-test, t=1.53, df=51, α=0.05, Table 4). However, the average C/N of HMW material from the femora (average = 26.3 ± 10.5) is significantly greater than that of the other Late Cretaceous terrestrial and aquatic vertebrates (average C/N of aquatic and terrestrial fossils = 8.4 ± 5.2; t-test,

t=7.63, df=45, α=0.05 and df=45, α= 0.05, respectively). Whereas these samples were obtained in a powdered form, there was no control of the removal of surficial contaminants. Despite the removal of low molecular weight material through dialysis, the C/N of the femora could reflect high molecular weight components from the associated sedimentary matrix that were not removed prior to grinding of the sample to a powder.

3.2 Ratios of amino acid enantiomers

3.2.1 Reproducibility

Although there are many reports of gas chromatographic analyses of N-PFP-isopropyl esters, no references were encountered for ion fragmentation patterns of PFP derivatives (Pollock, et al., 1977; Frank et al., 1977; Frank et al., 1978; Abe et al., 1983; Engel and Hare, 1985). This thesis presents ion fragmentation patterns and reproducibility for N-PFP-isopropyl esters of 14 amino acids (Appendix 2, Table 6).

Good reproducibility in the response of the MSD to individual enantiomers is observed among three injections of the standard mixture of amino acids containing 0.2nM of each enantiomer run under a single ion monitoring mode (Table 6). The coefficient of variation (CV) is less than or equal to 0.15 for most amino acid enantiomers and D/L

values. The CV for enantiomers and D/L values of alanine (Ala), isoleucine (Ile), leucine (Leu), aspartic acid (Asp), methionine (Met), glycine (Gly), Hypro, and Hylys is less than or equal to 0.10. The similarity in retention times for threonine (Thr) and valine (Val) and for glutamic acid (Glu) and phenylalanine (Phe) is a factor that is unique to these amino acids and contributes additional error to the integration result (chromatographic separation of enantiomers are illustrated in Appendix 3).

3.2.2 Enantiomer ratios of samples

The D/L of amino acids from the HMW material and TOF were characterized and compared. The D/L of amino acids in the HMW were expected to be non-racemic and to differ from those of the TOF. These expectations are consistent with previous observations.

The D-enantiomer of Hypro and Hylys was never observed in the analyses of HMW material isolated from fossils of Late Cretaceous vertebrates. Contributions of the L-enantiomer of these amino acids are discussed in section 3.3.5. Both the D- and L-enantiomers are most frequently detected for Ala, Leu, and Asp (Table 7). The response of the D- enantiomer of Thr, Val, Ile, serine (Ser), Pro, Glu and Phe is below the level of detection in the majority of cases. Lack of data for Ser, Pro, Glu, and Phe among many

samples (e.g. AMI-B-1, ORN-B-2, STE-B-1) is associated with high background during the latter half of the chromatogram. This interference obscured both the D- and L-enantiomers.

Amino acid D/L values of the HMW fraction from prehistoric bones and teeth are typical of high molecular weight material previously isolated from fossils (Weiner et al., 1976; Serban et al., 1988, Table 7). Such non-racemic mixtures may be a consequence of the HMW nature of the organic matter retained within the mineral matrix. High temperature simulations indicate that the extent of racemization is frequently lower for amino acids of a residual HMW fraction or humic-like material in comparison to the lower molecular weight components (Hare, 1980; Hoering, 1980; Kimber and Griffin, 1987).

Large differences in the enantiomer ratios of Asp, Glu, and Phe for the TOF and HMW material are observed for samples CER-B-2, CER-T-4, and HAD-B-1 (Table 8). For all cases, the D/L of Asp, Glu, and Phe for the TOF is twice as great as that obtained for the HMW component. The D/L of Asp from the HMW material is significantly different from that of the TOF (paired t-test, $t=11.32$, $df=2$, $\alpha=0.01$). In addition, the D/L of Asp, Glu, or Phe of the TOF is not included in the 95% confidence interval calculated for the D/L of the respective amino acid of the HMW material. Determinations of 95% confidence limits are based on the

standard deviation of replicate determinations of D/L values (Table 6). Similarly, the D/L values of amino acids of a total shell hydrolyzate were found to be significantly higher than the dialyzed fraction (Serban et al., 1988) These results suggest that high molecular weight fractions are less racemized than associated components composed of low molecular weight material and free amino acids.

Data for CER-B-2 and HAD-B-1 show that the D/L of Ala for the TOF also falls outside of the 95% confidence interval for the D/L of Ala for the HMW material (Table 8). In contrast to all other comparisons of D/L values between the TOF and HMW, the D/L of Ala is lower for the TOF than the HMW of CER-B-2. Variation in the rate of racemization among amino acids could account for the unique results for the comparison of the D/L of Ala between the TOF and HMW material of CER-B-2. Racemization rates among amino acids can be differentially affected by temperature, pH, and molecular structure.

The inability to resolve the majority of amino acid enantiomers for the TOF of sediments strongly inhibits comparisons of sediments and HMW material from fossils. There are no cases were D/L values can be compared for samples and sediments from the same sampling location. When the fossils are grouped, there is not a significant

difference in the average D/L of Ala between the TOF of the sediments and HMW material from vertebrate remains (t-test, df=27, α=0.05, Tables 7 and 9). Without direct comparisons of samples and sediments from the same microsite or bone bed, the data for the D/L of Ala may be inadequate for evaluating contamination in this study. The nearly two-fold difference between amino acid D/L values of the HMW material from tyrannosaur bone and the HMW material from the associated sediment would not be expected if contamination played a primary role.(Table 10).

3.3 Amino Acid Abundances

Data on yields and relative concentrations of amino acids assist in characterization of organic matter isolated from fossils and assessment of indigeneity. To this end, it is imperative to evaluate the amino acid fingerprints of modern precursors to the organic remnant that remains within ancient bones and teeth. These precursors include collagenous proteins and NCP. Further, comparisons between organic fractions from the prehistoric vertebrate remains and surrounding sediment can be a useful indicator of contamination.

3.3.1 Estimation of Secondary Amines

Amino acid compositions of primary amines were determined with HPLC. Without additional chemical manipulation only primary amines can be identified with the fluorescent agent, OPA. Consequently, estimates of concentration for the imino acids Pro and Hypro were based on GCMS. The abundance of Hylys was also determined by GCMS owing to poor resolution of Hylys by HPLC.

The concentration of amino acids from GCMS data can be determined by two methods. In one case, the amount of Pro, Hypro, or Hylys in a sample can be found from the relationship between concentration and response as defined by a calibration. Alternatively, estimates of concentration are based on knowledge of the relative proportions of Pro, Hypro, or Hylys observed from GCMS data and an amino acid of known concentration.

Estimates were not based on the first method as a consequence of two large sources of error. First, the precise relationship between concentration and response of the MSD changed with time as a function of variation in sensitivity. Shifts in sensitivity of the MSD were unpredictable and associated with fluctuations in the value of the electron multiplier. In addition, loss of amino acids could occur during all stages of derivatization and analysis of PFP-esters. Such losses could not be

accurately quantified. Consequently, the second method was chosen because, despite changes in sensitivity or evaporative loss, the relative response among amino acids should be less affected.

3.3.2 Yield of Amino Acids from Fossils

Only a very small portion of the HMW material isolated from Late Cretaceous fossils is composed of hydrolyzable amino acids. This is evidenced by the low values for yield in terms of amino acid weight and percent of the total weight that is amino acids (%AAWT), percentage of sample weight that is amino acid carbon and nitrogen, and percentage of total nitrogen and carbon that is derived from amino acids (Table 11). Concentrations of amino acids range from 0.02 to 0.39% or 1.5 to 29$\mu M \cdot g^{-1}$ of HMW material (Table 11). Expressed with respect to weight of bone, yields range from 1.35 to 1.5$\mu M \cdot g^{-1}$. This is at least 50% lower than concentrations from bones and teeth that are younger than 20,000 Ma but similar to previously reported data for Cretaceous fossils (Table 12).

The concentrations of amino acids do not appear to be related to fossil type or habitat of origin for the organism. There is no significant difference in the yield (%AAWT) between bones and teeth (t-test, df=11, α=0.05) nor between fossils from terrestrial and aquatic organisms (t-

test, df=31, α=0.05). For all samples a large fraction of the nitrogenous material is resistant to acid hydrolysis. This is evidenced by the small proportion of the total nitrogen that could be characterized as amino acids (0.1 to 5.3%, Table 11). These similarities suggest that the effects of diagenesis on the organic component are consistent among all fossils.

3.3.3 Reproducibility of Relative Concentrations of Amino Acids

Despite low concentrations of individual amino acids (less than 0.1 to 3.4 $\mu M \cdot g^{-1}$) analyses are highly reproducible (Figure 3, Table 13). Data for two ceratopsid teeth and one hadrosaur tooth indicates that, on average, duplicate analyses differ by 0.3 $\mu M \cdot g^{-1}$ (Table 13). In terms of mole percent the average difference is less than 3% for individual amino acids (Table 14). In the following discussion a difference in the concentration of an amino acid between two samples will be considered to be significant if it falls outside of the 95% confidence interval (average $\pm$ 2σ) for the average difference determined for the replicates (Table 14). Using this criteria, two measurements of concentration of an amino acid were considered to be dissimilar if they differed by more than 6.4 mole percent. This value represents the

maximum estimate of the 95% confidence (see data for Asp in Table 14).

3.3.4 Amino Acid Composition of Modern Bone Proteins

Collagens from modern bones and teeth are characterized by high concentrations of Pro and Gly and the presence of Hypro and Hylys (Table 15). In contrast, NCP have an abundance of Glu and Asp and little or no Hylys (Table 15). Among NCP, osteocalcin has a unique amino acid pattern that is characterized by the presence of both Hypro and γ-carboxyglutamic acid (Table 15). The HMW material isolated from a modern bone is similar in amino acid composition to collagen (Hare, 1980; Table 15).

3.3.5 Amino Acid Composition of Fossils

A common feature of the hydrolyzates of HMW material isolated from Late Cretaceous fossils is a depletion in basic amino acids relative to neutral and acidic (Tables 16,17). This was evident in many samples (e.g. AMI-B-1, PAR-B-1, CRO-T-1, CRO-T-3, ORN-B-1, ORN-B-2) even though several large unidentified peaks coeluted with and obscured the identification of histidine (His) and lysine (Lys) in other chromatograms. Interference from ammonia can occur within this region. Increased column pressure and retention time during the latter part of the chromatogram

suggests that high molecular weight compounds with strong affinity for the resin may also be eluting with the basic fraction. Owing to variation in resolution of basic amino acids, calculations of mole percentages and graphical representations are based on the acidic and neutral fractions (first 12 amino acids, Tables 18,19). In addition, calculations of mole percentages for all samples in a graphical comparison are based on a common set of amino acids. Consequently, an amino acid whose value was not determined for one sample was not included in the calculation of mole percent for all cases being compared.

The amino acid pattern of the HMW material is characterized by high concentrations of Gly and Glu (Figures 4,5,6,7; Tables 16,17,18,19 and references therein). These are the most abundant amino acids in 19 of the 38 fossils analyzed. Low concentrations of Hypro, (0.001 to 3.1 mole percent), were found in six bones (TEL-B-1, PAR-B-1, PLE-B-1, CER-B-1, HAD-B-1 TYR-B-1), and four teeth (CRO-T-1, CRO-T-3, TYR-T-1, and CER-T-1). Hydroxylysine was apparent in at least trace amounts in four of these samples. The presence of Hypro and abundance of Gly and Glu does not appear to be linked to fossil type or habitat of the organism (Figures 4,5,6,7; Tables 16,17,18,19). The abundance of Gly and the presence of Hypro and Hylys in the fossils are consistent with at least

a portion of the HMW material being derived from collagenous proteins. In this sense, the HMW material appears to have retained an indigenous signal.

The ability to isolate a component that is a remnant of an original organic fraction is related to the state of preservation of the fossil and the extraction procedure. The dialysis used in this study removes contaminants such as free amino acids and low molecular weight compounds that can easily migrate through fossils from the surrounding environment. Lower yields of total amino acids from HMW material relative to the TOF are probably related to loss of the low molecular weight contaminants and, possibly, breakdown products of the indigenous component during dialysis (Table 20).

There is also a difference in the relative concentrations of individual amino acids between the TOF and HMW material of fossils (Table 21, Figures 8 and 9). The following will identify the individual amino acids that show pronounced (more than 10%) differences. There is an increase in the relative contribution of Gly and Ala and a decrease in Val in the HMW material relative to the TOF of TYR-T-1. An increase in the proportion of Gly and decrease in Ala is observed in the HMW material of HAD-B-1 relative to the TOF. Although not significantly different (base on criteria established in Section 3.3.3), the HMW

material from the ceratopsid tooth had elevated levels, approximately 5 mole percent, of Thr and Lys and a reduced level, 6 mole percent lower, of Ile, in comparison to the TOF.

There is not sufficient comparative data to make generalizations regarding the shifts in the relative abundance of individual amino acids associated with dialysis. However, there was a significant decreases in yield in the HMW material relative to the TOF and changes in the relative abundance of amino acids were observed. The consistently high abundance of Gly and Glu in the HMW material of many of the samples suggests a similarity in the geochemical nature of the HMW material recovered from dialysis.

3.3.6 Comparison of Amino Acid Compositions Between Sediments and Sediments and Fossils

Contaminants to fossils can originate from the surrounding sediment matrix. Low molecular weight (LMW) materials contained in TOF of sediments can easily migrate through fossil materials, condense to form HMW compounds, and obscure the geochemical signal of an indigenous HMW organic component (Schroeder and Bada, 1976). This amino acid composition of the LMW fraction of the sediment was estimated by determining the difference in the actual

concentration of individual amino acids between the HMW and TOF. Assuming no specific binding, the difference in the relative concentrations of individual amino acids between the HMW material of a fossil and the LMW and HMW material of the surrounding sediment argues against simple contamination.

Among the five sediments from the Judith River Formation of Dinosaur Provincial Park, the relative abundances of amino acids in the TOF do not show a consistent pattern (Table 22, Figure 10). In contrast, three of five samples of HMW material from sediments have a similar signature (Table 23, Figure 11). In order of decreasing abundance, the three dominant amino acids in these three cases are Gly > Ala > Ser in the HMW component.

Differences in amino acid composition between the HMW and TOF of sediments were most noticeable for Glu and Ser. Within two of the sediments (SED-1 and SED-2), the relative proportion of Ser in HMW component is significantly greater than in the TOF (Figure 12). In these same two samples, the percent contribution from Glu is significantly less in the HMW material than the TOF. Sample SED-3 has a significantly lower concentration of Ser in the HMW component than the TOF.

There are significant differences between the amino acid signature of the sedimentary fractions and that of HMW

material of the fossils (Tables 18,19,20,21,22,23,24; Figures 13 to 18). The following discussion of these data, again, assumes that no specific binding has taken place. Additional experimentation would be required to test this possibility.

The concentration (mole percent) of many of the individual amino acids is significantly different (more than 10% is significant, see Section 3.3.3) in the comparison of HMW material from the fossils to the LMW component of the sediment. The following points out the most salient contrasts. An increase of more that 10 mole percent is observed in the concentration of Thr from LEP-S-1 and MET from AMI-B-1 relative to the LMW fraction of the associated sediment. There are also large reductions (more than 10%) in the level of Ser from AMI-B-1 and LEP-S-1, Asp from LEP-S-1, and Gly from TEL-B-1 relative to the LMW component of the sediment.

Comparisons between the HMW material from the sediment and fossil also show significant differences in concentration (mole percent) for many of the amino acids. One of the most noticeable differences in the comparison of the HMW fractions is a large decrease (more than 10 mole percent) in the relative abundance of Ser in AMI-B-1, LEP-S-1, and CER-B-3 in comparison to the sediment. In addition, the teleost TEL-B-1 has higher percentages of

Asp and Glu and the ceratopsid CER-B-3 has a higher mole fraction of Gly than the associated sedimentary matrix. These differences between the fossil material and the LMW and HMW organic components of sediments imply that, in the absence of specific binding, the HMW material of the fossil has a unique origin and is not merely a simple diagenetic product that has an organic precursor derived from the sediment.

3.3.7 Effects of the State of Preservation on Amino Acid Composition

The ability to obtain a non-contaminated indigenous component may be related to the state of preservation (degree of replacement, porosity etc) of the fossil. A geochemical comparison was made between a sample that was nonporous and had little replacement and a highly replaced porous section from the ceratopsid bone CER-T-3 (Table 25, Figure 19). This was done to differentiate the effects of dialysis and fossil quality on the amino acid yield and pattern of the HMW material. The concentration of amino acids in the porous sample is more than 4 times greater than that of the non-porous bone. No significant differences were found between the porous and non-porous bones in the concentration of individual amino acids. The elevated yield of amino acids from the porous bone

relative to the nonporous sample may be associated with an increased level of contamination. A 2°/$_{oo}$ difference in the nitrogen isotope value between the nonporous bone (-1°/$_{oo}$) and porous bone (+1°/$_{oo}$) also indicate different origins of the HMW organic fraction isolated from the two samples. These findings suggest that the geochemical characteristics of a fossil may be related to the state of preservation of the fossil. Porous bone is more likely to contain contaminants which could obscure the geochemical signal retained by an indigenous organic fraction.

3.3.8 Integrated Discussion of Amino Acid Data

The organic matrices within osteological and dental remains undoubtably undergo changes with time. As collagen in fossils degrades, the remnant proteins or peptides become enriched in acidic amino acids (Hare, 1980; Masters, 1987; Tuross et al., 1988). The high concentrations of Glu in the HMW material from fossils analyzed in this study are consistent with this trend. Owing to the affinity of hydroxyapatite for macromolecules that contain carboxyl groups, increases in the abundance of an acidic amino acid could stabilize the residual organic matter (Bernardi and Kawasaki, 1968).

The HMW component remaining in the Cretaceous fossils is also characterized by an abundance of Gly and, in some

cases, the presence of Hypro and Hylys. Differences between this material from the vertebrates and the organic components from associated sediments argues against contamination. The HMW fraction from remains of Late Cretaceous vertebrates may likely be a non-proteinaceous alteration product derived from both collagenous and noncollagenous proteins that have become stabilized owing to their association with the mineral phase.

3.4 Carbon and Nitrogen Isotope Data

3.4.1 Isotopic Values of Late Cretaceous Vertebrates

With the exception of bones from the hadrosaur femora size series, and samples CER-B-3 and DIL-B-1, $\delta^{15}N$ of HMW organic material isolated from Late Cretaceous fossils fall within the range previously reported for collagen from modern herbivores and carnivores (Table 26; Schoeninger, 1985; Schoeninger and DeNiro, 1984; Katzenberg, 1989). The $\delta^{13}C$ of the HMW component of aquatic and terrestrial vertebrate remains are similar to or slightly depleted relative to modern analogs (Table 26; Schoeninger, 1985; Schoeninger and DeNiro, 1984; Katzenberg, 1989) Carbon and nitrogen isotopic compositions of the fossils of marine animals fell within the range of $\delta^{13}C$ and $\delta^{15}N$ for terrestrial organisms. Consequently, $\delta^{13}C$ or $\delta^{15}N$ could not be used to distinguish between these two groups. As

discussed below (section 4.0) the depletion of $\delta^{13}C$ and $\delta^{15}N$ in the mosasaurs and sharks relative to modern counterparts may be related to isotopic depletions in sources of Late Cretaceous primary production.

Differences in the biochemical composition of the HMW component and that of collagen could explain the slight depletions in $\delta^{13}C$ for HMW material from non-marine fossils. High molecular weight noncollagenous organic matter has previously been shown to be depleted in $\delta^{13}C$ relative to the collagenous component (DeNiro and Weiner, 1988). It has been suggested that this trend could result from a higher concentration of ^{13}C depleted noncollagenous proteins or lipid in the HMW noncollagenous fraction (DeNiro and Weiner, 1988). Alternatively, selective incorporation of ^{12}C during the formation of condensation products could account for the observed depletion in $\delta^{13}C$.

With the exception of the hadrosaur femora data, bones and teeth of the same taxa are similar in their isotopic composition (Table 26, 27). There is no difference in $\delta^{13}C$ or $\delta^{15}N$ between the bones and teeth of ceratopsids (t-test, t=0.67 and 0.34, respectively, df=6, α=0.01). Except for the ceratopsid bone, CER-B··3, within a taxa, the isotopic composition of a bone(s) falls within the range of $\delta^{13}C$ and $\delta^{15}N$ reported for the teeth. These results are in agreement with the amino acid data and

indicate that the effects of diagenesis on the organic component of fossils is similar for bones and teeth. Alteration products that are isotopically similar for both materials may be associated with a common starting material and degradative pathway. The suggested mechanism may involve breakdown and loss of collagen, the formation of a more resistant HMW material through condensation reactions, and strong bonding with the mineral phase.

3.4.2 Isotopic Composition of Samples From the Hadrosaur Femora Size Series

Owing to the inability to determine the degree of mechanical cleaning, the hadrosaur femora data are treated separately and will not be used in subsequent interpretations of trophic structure. Average $\delta^{13}C$ and $\delta^{15}N$ values of the HMW fraction from these bones (-23.6 ± 1.4°/$_{oo}$ and 2.5 ± 2.6°/$_{oo}$, respectively) do not differ significantly from those of other hadrosaur samples (-24.4 ± 1.0°/$_{oo}$ and 4.7 ± 0.5°/$_{oo}$ for $\delta^{13}C$ and $\delta^{15}N$, respectively; t-test, t=1.16 and 1.85 for $\delta^{13}C$ and $\delta^{15}N$, respectively, df=15, α=0.05; Table 26 and 27). However, $\delta^{15}N$ values are highly variable (σ = 2.6) and three of the twelve bones have $\delta^{15}N$ ($\delta^{15}N$ less than 0°/$_{oo}$) that are not similar to values previously reported for collagen extracts of modern herbivores (Schoeninger, 1985; Schoeninger and

DeNiro, 1984; Katzenberg, 1989).

The unusual $\delta^{15}N$ values could reflect a significant contribution from an organic contaminant. The significant difference in average C/N between the hadrosaur femora data set and the other hadrosaur bones analyzed in this study may also be related to an exogenous component (Section 3.2). These observations suggest that, in addition to dialysis, mechanical cleaning of the fossils may be an important step for removal of contaminants.

3.4.3 Effects of Dialysis on Isotopic Compositions

Data for eleven samples indicate that the HMW material differs from the TOF by $0.1°/_{oo}$ in $\delta^{13}C$ and $-2.9°/_{oo}$ in $\delta^{15}N$ (Table 28). A paired t-test shows no significant difference in $\delta^{13}C$ or $\delta^{15}N$ between the TOF and HMW material ($t<1.6$ for both $\delta^{13}C$ and $\delta^{15}N$, $df=8$, $\alpha=0.01$). However the average difference in $\delta^{15}N$ (-2.9) is much larger than the 99% confidence interval based on replicate analyses (average difference between replicates plus 4σ = $0.5°/_{oo}$). Results of the paired t-test may be misleading as this test does not take into account directionality. A difference of nearly $3.0°/_{oo}$ is generally considered a large discrepancy. The magnitude and direction of the $\delta^{15}N$ shift is not consistent among samples. This variability is likely to be related to the degree and type

of low molecular weight contamination that influences the signature of the TOF.

The uniqueness of the $\delta^{15}N$ values can also be demonstrated by comparison to literature values. Excluding enrichments in $\delta^{15}N$ observed among water deprived southern African herbivores, the high $\delta^{15}N$ of TOF of a ceratopsid, hadrosaur, and tyrannosaur (15.5°/$_{oo}$, 14.1°/$_{oo}$, and 14.9°/$_{oo}$, respectively) are unusual in comparison to modern herbivorous animals (Schoeninger and DeNiro, 1984; Ambrose and DeNiro, 1986; Sealy et al., 1987). The highest $\delta^{15}N$ for an individual herbivorous animals are reported by Ambrose and DeNiro (1986). These values range between 12 and 13°/$_{oo}$. The extreme $\delta^{15}N$ values from the TOF are likely to reflect contributions from exogenous low molecular weight materials. Low molecular weight contaminants can effectively be reduced by the dialysis procedure used in this study.

3.4.4 Fossil Plant and Sediment $\delta^{13}C$ and $\delta^{15}N$ Values

Isotopic compositions of fossil trees fall within the range of previously reported values for modern flora (Table 29). Values of $\delta^{13}C$ and $\delta^{15}N$ for modern trees range from -23 to -30 and -2 to +6, respectively (Hoering, 1955; Wada, et al., 1975; Shearer and Kohl, 1978; Deines, 1980; Virginia and Delwiche, 1982). The entire range of $\delta^{15}N$ for

terrestrial flora (-7 to +10) is more extreme. Owing to the lack of Late Cretaceous floral material, interpretations of isotopic compositions of primary producers for ancient food web analysis must rely on data for modern plants.

The isotopic compositions of the TOF of five sediment samples are similar (average values: $-24.6 \pm 0.6^{o}/_{oo}$ and $6.3 \pm 0.9^{o}/_{oo}$ for $\delta^{13}C$ and $\delta^{15}N$, respectively; Table 29). In comparison to the TOF, the HMW material is not different in $\delta^{13}C$ (paired t-test, t=-0.47, df=8, α=0.05) but is significantly different in $\delta^{15}N$ (depleted by $4.5^{o}/_{oo}$; paired t-test, t=6.1, df=8, α=0.05). The incorporation of the light isotope in the HMW fraction could be associated with kinetic isotope effects during the formation of this material. As a consequence of such fractionation, there is a greater probability that a shift will be observed for $\delta^{15}N$ than for $\delta^{13}C$. Owing to the high abundance of carbon relative to nitrogen a change in structure will affect the $\delta^{13}C$ more readily than $\delta^{15}N$.

Close agreement between $\delta^{13}C$ and $\delta^{15}N$ for sediments and fossil remains could indicate contamination. Although average $\delta^{13}C$ and $\delta^{15}N$ for the TOF and HMW material from the sediments overlap with the range for fossils, the $\delta^{15}N$ of faunal remains and sediments from the same bone bed are different (Figure 20). Comparisons indicate that shifts in

$\delta^{15}N$ of the fossils range from -3.0 to +3.8°/$_{oo}$ relative to TOF and 1.8 to 11.1°/$_{oo}$ relative to the HMW material of the associated sediment. Such large distinctions suggest that the origin of the HMW material isolated from vertebrate remains is unique from that derived from sediments.

4.0 Interpretation of Food Web Structure

This interpretation is assisted by isotopic comparisons to modern analogs and the previous evaluations of dietary habits. Within a particular taxon, there are many factors such as size and maturity that can result in isotopic variability among individuals. The following discussion of trophic hierarchy assumes that the fossils that have been analyzed are from adults. Only in one case, an immature tyrannosaurid, was an exception clearly made. In addition, the isotope signature of a particular fossil or an average of all individuals from a single taxa is assumed to be a representative value for the taxon.

Repeated analyses of ceratopsids, tyrannosaurs, hadrosaurs and crocodiles indicate that variability among individuals can exist within a taxon (ceratopsids and crocodiles). Clearly, additional analyses will provide a more accurate interpretation of trophic position for a particular taxonomic group. The following will demonstrate that, based on present knowledge of modern ecology, as well as the ecology of Late Cretaceous vertebrates, the trophic hierarchy delineated by isotope data represents a logical framework for interpretations of energy flow.

Within modern systems terrestrial and aquatic consumers can have similar $\delta^{13}C$ and $\delta^{15}N$ values (DeNiro, 1985; Schoeninger and DeNiro, 1984). This was also

observed for In contrast, marine organisms usually differ from terrestrial and aquatic consumers in both $\delta^{13}C$ and $\delta^{15}N$ (Schoeninger and DeNiro, 1984). Late Cretaceous marine consumers do not differ in $\delta^{13}C$ or $\delta^{15}N$ from ancient aquatic or terrestrial animals.

Similarity of marine values to aquatic and terrestrial systems ($\delta^{13}C$ less than $-23^{o}/_{oo}$) could be related to the $\delta^{13}C$ and $\delta^{15}N$ of the primary producers that supply carbon and nitrogen to the marine system. Low $\delta^{13}C$ values have frequently been observed for marine organic matter in Cretaceous sediments (Dean et al., 1986; Popp et al., 1989; Rau et al., 1989). Such depletions have been attributed to elevated atmospheric, and thus oceanic, CO_2 partial pressures (Arthur et al, 1985; Dean et al., 1986; Knoll et al., 1986).

The explanation for $\delta^{13}C$ depleted organic matter during the Late Cretaceous is related to the magnitude of the change in $\delta^{13}C$ that occurs between the plant and the inorganic carbon reservoir (CO_2 pool, see Fogel and Cifuentes and references within for various aspects of the information treated in the following two paragraphs). The $\delta^{13}C$ of plants frequently exhibit a $-20^{o}/_{oo}$ shift relative to their inorganic carbon source (Oceanic CO_2 = $0^{o}/_{oo}$, atmospheric CO_2 = $-7^{o}/_{oo}$). This isotopic fractionation occurs during photosynthesis during diffusion of CO_2 into

the plant (apparent fractionation = -4.4°/$_{oo}$) and during enzymatic carbon fixation (apparent fractionation = -29.4°/$_{oo}$) The observed $\delta^{13}C$ of plants is a consequence of both diffusion and carboxylation.

When the pool of CO_2 is not limiting, the $\delta^{13}C$ of the plant is primarily controlled by the isotopic fractionation that occurs during enzymatic incorporation of carbon. This could be as negative as -36°/$_{oo}$. In comparison to terrestrial plants, aquatic and marine phytoplankton are more sensitive to diffusional processes because CO_2 diffuses more slowly in water than air. In high concentrations of CO_2, cells exhibit large fractionations, between the $\delta^{13}C$ of the cells and the inorganic carbon reservoir. This isotopic shift is similar to those observed in terrestrial plants. Similarly, high partial pressures of CO_2 during the Late Cretaceous could effectively lower the $\delta^{13}C$ of marine phytoplankton.

Late Cretaceous sediments also exhibit reduced $\delta^{15}N$ (less than 1°/$_{oo}$; Rau et al., 1987). The occurrence of low $\delta^{15}N$ is thought to be associated with the dominance of nitrogen fixation among phytoplankton.

Alternatively, inputs from terrestrial environments could result in $\delta^{13}C$ and $\delta^{15}N$ that are similar in marine and terrestrial signatures. Values ranging from -21 to -24°/$_{oo}$ for $\delta^{13}C$ and 6 to 9°/$_{oo}$ for $\delta^{15}N$ are typical for

consumers from subtropical mangrove systems and overlap with isotopic compositions of consumers raised on terrestrial diets (DeNiro and Epstein, 1978; Harrigan et al., 1989). Owing to the overlap in isotope values of marine, terrestrial, and aquatic consumers, the placement of organisms within habitats requires supportive paleoenvironmental information. As in modern food webs, the $\delta^{15}N$ of vertebrates from terrestrial and aquatic habitats increase along a trophic continuum (Table 26, Figures 21,22). Of the two isotopes, $\delta^{15}N$ signatures are a much stronger indicator of trophic position. Thus, interpretations of feeding hierarchies will focus on nitrogen isotope signatures.

For ease of discussion, a preliminary interpretation will be made based on the isotopic distributions of terrestrial megafauna. Considerations of mesofauna will, subsequently, be added. For similar reasons, aquatic organisms are grouped according to inland and coastal tendencies.

4.1 Terrestrial Food Web

Within the entire terrestrial community, there is, generally, little variation in $\delta^{13}C$ among organisms of different trophic levels. Such small shifts between consumers and diets have previously been observed (Fry and

Sherr, 1984; Harrigan et al., 1989). Isotopically depleted values, e.g. -27°/$_{oo}$ for a nodosaur, could reflect a unique dietary source. Examples of modern taxa with $\delta^{13}C$ of less than -27°/$_{oo}$ include Equisetum, Cycas, Saggittaria, and Scirpus (Smith and Epstein, 1971; DeLuane, 1986; Chmura et al., 1987).

With the exception of ceratopsians, the food web structure of the terrestrial system concurs with previously proposed views of the dietary habits of these organisms (Norman, 1985). The $\delta^{15}N$ values of terrestrial megafauna increase in the order nodosaur < hadrosaur < ceratopsid < nodosaur < tyrannosaur (Table 26, Figure 21). The more depleted values for hadrosaurs and one nodosaur are consistent with traditional views that nodosaurs and hadrosaurs were primary consumers and the high $\delta^{15}N$ of the tyrannosaur relative to these herbivores is typical of a carnivore.

The enriched average $\delta^{15}N$ of the ceratopsid, an acclaimed herbivore, relative to hadrosaurs and the nodosaur may reflect a distinction in feeding habits between these species. Differences in the morphological features and mechanical efficiency of ceratopsian dental apparatus relative to other herbivores is also indicative of a different food source (Ostrom, 1966).

Variations in $\delta^{15}N$ among individual ceratopsids imply

that these animals may have fed on a wide variety of isotopically distinct primary producers. This might occur as a consequence of selective feeding or the distribution of individuals among habitats that are dominated by different types of vegetation. For example, reported $\delta^{15}N$ for ferns, mosses, lichens, and clover are less than $0^{o}/_{oo}$ whereas large trees have values as high as $6^{o}/_{oo}$ (Hoering, 1955; Wada et al., 1975; Shearer and Kohl, 1978; Virginia and Delwiche, 1982). Variations in the isotopic compositions of primary producers could result in a wide range of $\delta^{15}N$ among herbivores.

The teeth of nodosaurids are not arranged into a specialized cutting battery and are limited to the posterior portion of the mouth. This arrangement is in contrast to ceratopsids whose compact dentary enables grinding. The short, broad, and laterally compressed teeth of nodosaurs also differ from the longer and more robust dentition of both ceratopsids and hadrosaurs. Variation in diet among herbivorous taxa is suggested by contrasting dental morphologies.

Two samples of nodosaurs teeth differ in isotopic composition. One nodosaurid, NOD-T-1 has a much higher $\delta^{15}N$ and $\delta^{13}C$ (6.9 and $-23.9^{o}/_{oo}$, respectively) than the other PAN-T-1 (2.3 and -27.0 for $\delta^{15}N$ and $\delta^{13}C$, respectively). Such distinctions could arise as a

consequence of differences in the isotopic composition of the plants that contribute to the diet, insectivory, or opportunistic feeding on protein enriched dietary sources. The $\delta^{15}N$ of a extant insect from south Florida is $8.5^{o}/_{oo}$ (P.H. Ostrom, unpublished data). In the present environment, a dietary contribution from this type of insect could result in an enrichment in the $\delta^{15}N$ of a consumer relative to terrestrial herbivores. The average $\delta^{15}N$ reported by Schoeninger and DeNiro (1984) for terrestrial herbivores is $5.3^{o}/_{oo}$.

Among the mesofauna, Stegoceras and Paleosaniwa have the lowest $\delta^{15}N$ values (Figure 21). The similarity in the $\delta^{15}N$ of the stegoceras and hadrosaur is consistent with a plant based diet. The relatively depleted $\delta^{15}N$ of the Paleosaniwa and didelphid suggests that these individuals were not entirely carnivorous. There appears to be no definitive evidence of feeding habits for these organisms. Additional isotopic data on Late Cretaceous lizards and mammals may assist in more clearly defining the diets of Paleosaniwa and didelphid.

The large difference in the $\delta^{15}N$ of two ornithomimids could, very well, be associated with the omnivorous behaviors that had been attributed to these dinosaurs (Norman, 1985; Russell, 1989). Selective feeding on eggs, small animals, insects, or fruit would result in isotopic

distinctions between individuals.

The huge sickle claw on the upper appendage, arrangement of muscles that produced a powerful bite, and the backward curvature of the teeth distinguish dromaeosaurs as top predators (Norman, 1985). High $\delta^{15}N$ ($7.9°/_{oo}$) also characterizes dromaeosaurs as a carnivores. The $1.3°/_{oo}$ enrichment of this dinosaur relative to the average $\delta^{15}N$ for tyrannosaurs is, perhaps, indicative of a distinction in predation strategies. Without the size advantage of a tyrannosuar (6 to 14m), dromaeosaurs (maximum 3 to 3.3 m) may have hunted in packs, targeted sick or older individuals, or eaten carrion. Thus, many species provided dietary opportunities for dromaeosaurs. Tyrannosaurs may have used a stalking strategy and, through learned behaviors, focused on a single species such as a hadrosaur. This would have been a particularly successful method during the Late Cretaceous of southern Alberta when certain herbivores (hadrosaurs) dominated.

Exploitation of sick, injured or young individuals would also have been an effective tactic for young tyrannosaurs. A more varied diet could explain the enriched $\delta^{15}N$ ($11.4°/_{oo}$) of the immature individual relative to the adults (average $\delta^{15}N = 6.6°/_{oo}$, Table 26).

4.2 Aquatic Food Web

Based on descriptions from both Brinkman (in press) and Russell (1989), aquatic vertebrates can be separated into a coastal or an inland inhabitants (Figure 22). However, there is no $\delta^{13}C$ or $\delta^{15}N$ distinction between these two groups. Although it is not uncommon for isotope signatures to overlap between coastal and inland communities, similarities could arise as a consequence of interactions between the inhabitants of the two environments. Whereas it is difficult to distinguish a clear grouping on the basis of $\delta^{13}C$, interpretations of trophic structure can be inferred from $\delta^{15}N$ data.

The coastal group includes taxa that may have migrated between inland and salt waters. The coastal assemblage includes Aspideretes, pavement toothed sharks (Hybodus), Myledaphus, Paratarpon, Paralbula, crocodiles and plesiosaurs. Members of the inland community are Acipenser, champsosaurs, Scapherpeton, lepisosteids, teleosts, and Amia.

4.2.1 Aquatic Inland Community

Trophic structure among inland consumers shows a grouping of organisms that have $\delta^{15}N$ values that are approximately $7^{o}/_{oo}$. The similarity in $\delta^{15}N$ values suggests that the gar (lepisosteid) and medium sized teleost fish

may have targeted similar prey items including small aquatic vertebrates and invertebrate species. This may not have been the diet selected by Scapherpeton although this long bodied salamander may have been fully aquatic (D. Brinkman, personal communication). Nitrogen isotope values do not offer a clear indication of the feeding tendency of Scapherpeton.

It is clear, based on the elevated $\delta^{15}N$, that Amia may have chosen among teleost, lepisosteid, and salamander as food sources (Figure 22). In contrast, low $\delta^{15}N$ of the Acipenser are consistent with detritivorous tendencies attributed to this organism (Estes, 1964). The view that a champsosaur was piscivorous is not in disagreement with the isotope data despite a slight depletion ($1^{o}/_{oo}$) of its $\delta^{15}N$ relative to that of the fish. Differences in prey size could render minor differences in $\delta^{15}N$ observed between medium sized fish and champsosaur.

The trophic structure of the inland coastal community does not differ markedly from that of a modern subtropical ecosystem (Table 30, Figure 23, P.H. Ostrom, unpublished data). Small fish, Gambusia, Lucania, and Poecilia are isotopically similar ($\delta^{15}N$ approximately $8.8^{o}/_{oo}$). Diets are primarily influenced by insects (Odum and Heald, 1972; W. Loftus, Fishery Biologist, Everglades National Park, Florida, personal communication). These consumers are

bracketed by the bottom feeder, Ictalurus, and the omnivorous sunfish Lepomis. The predatory nature of the lepisosteid is consistent with an elevated $\delta^{15}N$.

The isotopic similarity of fish with a common diet, Gambusia, Lucania, and Poecilia, is comparable to the grouping observed among medium sized piscivorous fish from the Late Cretaceous. As indicated by dietary preference and $\delta^{15}N$, Ictalurus and Acipenser share a common trophic position in the modern and prehistoric food webs, respectively. A comparison of the $\delta^{15}N$ of Lepomis and the insectivorous fish demonstrates the sensitivity of isotope values to small changes in diet. Unlike the insectivores, diets of Lepomis are more variable and may include prawns and amphipods. This slight shift in dietary preference is concomitant with a $1^{o}/_{oo}$ shift in $\delta^{15}N$. Positioning of top predators in modern and ancient food webs is reflected in higher $\delta^{15}N$ values.

4.2.2 Aquatic Coastal Community

Among members of the coastal community analyzed in this study, Aspideretes and Paratarpon are at the lowest position ($\delta^{15}N$ approximately $4.7^{o}/_{oo}$) in the trophic hierarchy. This position could reflect the affinity of these animals for invertebrates. Modern relatives of both species consume crustaceans (Harrington and Harrington,

1960; Halliday and Adler, 1987). Variation in the nitrogen isotope values of crocodiles may be recording differences in feeding habits that occur with age or between individuals. The difference between the $\delta^{15}N$ of Aspideretes and the average for the crocodile ($2.6^{o}/_{oo}$ difference) closely approximates the observed trophic fractionation between an organism and its diet (Wada et al., 1975; Harrigan et al., 1989). Nitrogen isotope data appear to corroborate previous views of the feeding habits of Late Cretaceous crocodiles (Russell, 1989). Modern crocodiles have varied diets ranging from fish to large birds and mammals (Cott, 1961). Variation in the $\delta^{15}N$ of Late Cretaceous crocodiles may be related to differences in feeding habits among individuals.

By analogy to the modern ray, Hypolophus sephen, Myledaphus, may have had affinities for crustaceans and shellfish (Estes, 1964). The enriched $\delta^{15}N$ value of Myledaphus, $6.4^{o}/_{oo}$, relative to the detritivores, e.g. Aspideretes, may appear unusual. However, this signature may be indicative of a unique source of nitrogen at the base of its food web. Within modern systems, $\delta^{15}N$ of freshwater phytoplankton are enriched relative to the terrestrial detrital component from the same area (Minigawa and Wada, 1984; Ostrom and Macko, submitted). A phytoplankton base that supplies nutrients to Myledaphus

via filter feeders could account for the nitrogen isotopic composition of this organism.

Shell fish may also have been consumed by Paralbula (Russell, 1989). As with Myledaphus, the $\delta^{15}N$ of the shell fish predator, Paralbula, could be related to the nitrogen source that supplies nutritional support to the filter feeders that it consumes. The influence of isotopically enriched marine organic matter could be possible owing to the potential marine affinity of this animal (D. Brinkman, personal communication).

The above argument complements traditional views of feeding habits of Paralbula. Alternatively, the enrichment in $\delta^{15}N$ of Paralbula relative to Myledaphus could be associated with differences in dietary composition. In comparison to Myledaphus, Paralbula may have consumed higher trophic level organisms.

The pavement-toothed shark is another organism that is apparently adapted for feeding on shell fish. The solid crushing surface of their dentition could be particularly useful for acquiring muscle tissue from shell fish (Romer, 1966). Despite the similarity in adaptations for feeding between the pavement-toothed shark and Myledaphus, or Paralbula, $\delta^{15}N$ of the shark differ from these consumers. Such contrasts in nitrogen isotope signatures suggest that the diet of pavement-toothed sharks was not identical to

either Paralbula or Myledaphus.

The plesiosaur at the apex of the trophic hierarchy concurs with the piscivorous tendencies of this animal. The presence of large tidal channels during the Late Cretaceous allowed plesiosaurs to migrate between oceanic and inland habitats. In either ecosystem, the $\delta^{15}N$ values of consumers are consistent with a pattern of energy flow leading to the plesiosaur via a detritus or plankton based food chain consisting of filter feeders, shell fish consumers, and various sized insectivorous and piscivorous fish.

The variation in $\delta^{13}C$ may reflect affinities for particular microhabitats that differ in the species of primary producer that dominate. More intensive and systematic sampling could assist in evaluating this possibility.

4.2.3 Marine Consumers

All marine fossils were obtained from a distinct formation from those of the terrestrial and aquatic samples. Consequently, the marine organisms may not be comparable to the aquatic and terrestrial fauna. The most noticeable feature of these data are the depleted $\delta^{13}C$ values. A possible explanation of these signatures, in terms of organic carbon sources, has already been put

forth (Section 4.0).

The $\delta^{15}N$ of the mosasaurs and shark are depleted relative to values of aquatic consumers. This supports the supposition that isotopic compositions of organic matter at the base of the marine food web differed from that of the aquatic system. Clearly, lack of analyses on organisms of various trophic levels limits the ability to make accurate interpretation of trophic position for marine consumers based on isotope data.

4.2.4 Overview of Food Web Interpretations

Within individual food webs the isotopic composition of Late Cretaceous fossils can be used to define trophic structure. Plausible suggestions of specific feeding relationships and strategies were possible based on $\delta^{13}C$ and $\delta^{15}N$ signatures. Both the data and interpretations were, generally, consistent with many trends that have been observed in modern systems and traditional views of the ecology of these prehistoric communities. Such consistencies suggest that an indigenous signal has been retained in the HMW component of the fossils.

4.2.5 Discussion of Variability in Isotopic Results

The largest variability within a taxa was observed among the ceratopsids. Similar variability can also be

observed within modern taxa. In the modern environment, differences in isotopic compositions are primarily a function of food source (Harrigan et al., 1989; Minagawa and Wada, 1984). However, differences in $\delta^{15}N$ or $\delta^{13}C$ among fossil material could be related to both diagenesis and feeding preferences.

Isotopic variation associated with diet could be tested by comparing fossils from different paleoenvironments within which food sources may have differed. In that feeding relationships are a function of community structure, knowledge of the paleoenvironment from which a a fossil was obtained will assist in constraining interpretations of isotope data. The relationship between diagenesis and variation in $\delta^{13}C$ and $\delta^{15}N$ is difficult to test. Comparisons of data among non-porous samples from different environments of deposition may assist in this evaluation.

4.2.6 Future Research

Several important questions have developed throughout the discussion of the isotope results and these will require future research. As discussed above (Section 4.2.5) it will be important to address the relationship between isotopic variability and diagenesis. Overlap in $\delta^{13}C$ and $\delta^{15}N$ among marine, terrestrial, and aquatic

communities limits interpretations. In this regard, data sets can be strengthened through a systematic sampling strategy. The strategy should be to constrain outcomes by collecting fossil remains from distinct paleoenvironmental settings. In this way, small isotopic variations associated with habitat differences may become apparent. The understanding of the low $\delta^{13}C$ values of marine fossils is particularly dependent on this approach.

5.0 CONCLUSIONS

A set of hypotheses were presented in section 1.8 of the introduction of this thesis. The following presents the findings of this thesis with respect to these hypotheses. A concise explanation is also given. After these findings are listed, the important conclusions and implications are discussed.

Yield of HMW Material

1. The yields of HMW material from Late Cretaceous vertebrates in this study are similar to the yields reported for fossils of Pleistocene age or older. This is consistent with thermal alteration experiments and previous results which indicate loss of organic material in bones and teeth over time.

C/N Values

1. The C/N of the HMW material from fossils analyzed in this study is higher than the C/N of collagen and NCP but similar to the C/N of organic matter retained in mineral aggregates analyzed by DeNiro and Weiner (1988). The HMW material from fossils probably differs from modern proteins because it is a long term degradation product. Independence of the $\delta^{15}N$ and $\delta^{13}C$ from C/N suggests that C/N data

may not provide a useful criteria for evaluating isotope data.

2. The average C/N of samples of the hadrosaur femora size series (samples obtained as a powder) is significantly greater than that of other Late Cretaceous vertebrates. These data suggest that mechanical cleaning may be important for removal of contaminants.

Enantiomer Ratios (D/L values)

1. The amino acids from HMW material from the fossils in this study are non-racemic (all less than 0.27). These D/L values are consistent with the results of high temperature simulations which show that the extent of racemization is low for amino acids of a residual HMW fraction.
2. The enantiomer ratios of Asp, Glu, and Phe are significantly lower in the HMW than the TOF of fossils. This observation is consistent with the results of Serban et al. (1988) and suggest that HMW fractions are less racemized than an associated LMW component. The D/L of Ala from the HMW material of fossils is significantly different than the associated TOF. In one comparison the D/L of the HMW fraction was greater than the TOF. This unique result could be related to variation in the rate of

epimerization among amino acids.

3. Comparisons of D/L values of the HMW of fossils to the TOF of sediments were limited to data for Ala. No significant difference was observed in the average D/L of Ala between the HMW of the fossils and TOF of the sediments. These results may be inadequate for evaluating contamination as there were no cases where D/L values were obtained for fossils and sediments from the same location. However, the nearly two-fold difference between amino acid D/L values of the HMW from a tyrannosaur bone and HMW material from the associated sediment argues against contamination.

Amino Acid Abundances

1. The yield of amino acids from the HMW fraction of the fossils in this study is similar to the yield obtained from organic matter isolated from Cretaceous fossils in previous studies.
2. Similarly to collagen, the amino acid composition of the HMW material is characterized by high concentrations of Gly and, in some cases, the presence of Hyp and Hyl. These results are consistent with at least a portion of the HMW material being derived from collagenous proteins.

3. The yield of amino acids from the HMW material is significantly less than that from the TOF. The relative concentrations of amino acid in the HMW material differ from that of the TOF. Both of these results are consistent with loss of low molecular weight contaminants, and possibly, breakdown products of the indigenous component during dialysis.

4. A and B:

   The yield and relative concentrations of amino acids differ between the HMW material of the fossils and the LMW and HMW component of the sediments. These differences imply that, in the absence of specific binding, the HMW material of the fossil is not, merely, a simple diagenetic product that has an organic precursor derived from the sediment.

   C.

   The yield of HMW material from a porous bone was four times as great as the yield of HMW material from a non-porous segment of the same bone. This may be indicative of increased levels of contamination in the porous bone relative to the non-porous bone. The porous segment had a significantly higher concentration of Glu than

the non-porous segment. This distinction may indicate a difference in the origin of the HMW material within the two samples.

Stable Isotope Data

1. With the exception of samples from the hadrosaur femora size series, and CER-B-3 and DIL-B-1, the $\delta^{15}N$ of the HMW material isolated from fossils fall within the range previously reported for collagen from modern organisms. Carbon isotope values are similar or slightly depleted relative to modern analogs. These results are consistent with the retention of an indigenous signal by the HMW material.
2. Nitrogen isotope values are good indicators of trophic level. For example, primary consumers within aquatic and terrestrial habitats are depleted in $\delta^{15}N$ relative to carnivores from the same food web. The ability to document trophic structure within the ancient food webs is consistent with the retention of an indigenous signal by the HMW material.
4. A.

   The HMW material from hadrosaur bones received as a powder differed in $\delta^{15}N$ from HMW material prepared from whole bones or teeth of hadrosaurs. The $\delta^{15}N$

of some of the samples obtained as a powder were outside the range of values reported for modern consumers. These results suggest that mechanical cleaning may be an important step for removal of contaminants.

B.

The HMW material from the fossils was depleted in $\delta^{15}N$ relative to he TOF of fossils. The $\delta^{15}N$ of the TOF of many samples were outside the range of values reported for modern consumers. These results suggest that the dialysis may be another important step for removal of contaminants.

C and D.

The HMW material from the fossils differed in $\delta^{15}N$ from the HMW material and TOF of the associated sediments. These differences indicate that the origin of the HMW material isolated from vertebrate remains is unique from that derived from sediments.

The geochemical characteristics of HMW organic matter isolated from Late Cretaceous vertebrates are consistent with an indigenous origin. High concentrations of Glu and Gly and the apparent presence of hydroxyproline suggest that this material is a diagenetic alteration product,

possibly derived from collagenous and noncollagenous proteins, that has become stabilized owing to its association with the mineral phase. The non-racemic nature of the amino acid enantiomers from the HMW material is typical of residual high molecular weight organic fractions isolated from fossils. Distinctions between the HMW material of fossils and organic fractions isolated from sediments in terms of amino acid patterns and D/L values argues against contamination of the fossil by the surrounding environment of deposition. The similarity in isotope patterns between modern and Late Cretaceous food webs is strong evidence for the retention of an indigenous signal from the HMW material isolated from fossils.

The retention of an indigenous signal in the HMW organic fraction of Late Cretaceous fossils has tremendous implications. Given the existence of such material, many exciting problems may be approached. For example, applications for stable isotope tracing include comparisons of food web structure among different prehistoric communities, detailed analyses of organisms along environmental gradients such as those described by Brinkman (in press), and determination of trophic status among prehistoric organisms whose dietary habits are not well known. Analysis of the $\delta^{15}N$ and $\delta^{13}C$ of individual amino acids and amino acid enantiomers derived from an

indigenous component could assist in distinguishing differences in metabolism among taxa, the evolution of biochemical pathways, and could also provide additional criteria for indigeneity (see Ostrom and Fry, submitted for a detailed discussion).

Whereas a variety of biochemical analyses have been applied to fossils which are less than 10,000 years old, the results of this dissertation should stimulate the analysis of older well-preserved specimens. This multidisciplinary approach may unlock clues retained in fossils that will open new perspectives in the fields of geochemistry and paleontology.

Table 1. Late Cretaceous vertebrate samples and collection locations.

Specimen	Sample Code	Sample Type	Collection Location*
Aquatic Fish			
Amia (bowfin)	AMI-B-1	centra	JRF
Amia (bowfin)	AMI-B-1	centra	BB 100
Teleost	TEL-B-1	3 centra	BB 54
Lepisosteid (gar)	LEP-S-1	scales	BB 54
Lepisosteid (gar)	LEP-B-1	2 vertebrae	JRF
Myledaphus	MYL-T-1	2 teeth	BB 54
Paralbula	PAR-T-1	tooth plate	Iddisly
Paratarpon	PAR-B-1	maxilla	88.81.3
Hybodus	PTS-T-1	3 teeth	JRF
(Pavement tooth shark)			
Acipenser (sturgeon)		STU-T-1	spine JRF
Aquatic Reptiles			
Aspideretes			
(Trionychid turtle)	ASP-B-2	scute	JRF
Champsosaur	CHA-B-1	2 vertebrae	JRF
Champsosaur	CHA-T-1	8 teeth	BB 54
Plesiosaur	PLE-B-1	rib	JRF
Scapherpeton			
(salamander)	SCA-B-1	vertebrae	BB 54
Crocodile	CRO-T-1	1 tooth	JRF
Crocodile	CRO-T-2	1.5 teeth	JRF
Crocodile	CRO-T-3	1 tooth	JRF
Terrestrial Mammal			
Didelphid (opposum)	DIL-B-1	jaw	JRF
Terrestrial Mesofauna			
Dromaeosaur	DRO-B-1	phalanx	JRF
Ornithomimid	ORN-B-1	phalanx	JRF
Ornithomimid	ORN-B-2	phalanx	JRF
Paleosaniwa (lizard)	PAL-B-1	centrum	BB 100
Stegoceras	STE-B-1	skull	JRF

Table 1. (cont)

Specimen	Sample Code	Sample Type	Collection Location
Terrestrial Megafauna			
Ceratopsid	CER-B-1	phalanx	JRF
Ceratopsid	CER-B-2	phalanx	JRF
Ceratopsid	CER-B-3	rib	BB43
Ceratopsid	CER-T-1	1 tooth	JRF
Ceratopsid	CER-T-2	1 tooth	JRF
Ceratopsid	CER-T-3	1 tooth	JRF
Ceratopsid	CER-T-4	1 tooth	JRF
Ceratopsid	CER-T-5	1 tooth	JRF
Hadrosaur	HAD-B-1	phalanx	JRF
Hadrosaur	HAD-T-1	1 tooth	JRF
Hadrosaur	HAD-T-2	1 tooth	JRF
Hadrosaur	HAD-T-3	1 tooth	JRF
Hadrosaur	HAD-T-4	1 tooth	JRF
Nodosaur	NOD-T-1	3 teeth	JRF
Nodosaur	NOD-T-2	3 teeth	JRF
Panoplosaur	PAN-T-1	2 teeth	JRF
Tyrannosaur	TYR-B-1	phalanx	JRF
Tyrannosaur	TYR-T-1	1 tooth	JRF
Tyrannosaur	TYR-T-2	1 tooth	JRF
Tyrannosaur (immature)	TYR-T-3	1 tooth	JRF
Marine Fauna			
Mosasaur	MOS-B-1	vertebra	NB
Mosasaur	MOS-T-1	1 tooth	NB
Mosasaur	MOS-T-2	1 tooth	BP
Shark	SHA-T-1	1 tooth	NB

* Abbreviations for collection locations are:
JRF Judith River Formation, Dinosaur Provincial Park (DPP), Alberta
BP Bear Paw Formation, Drumheller, Alberta
NB Niobrara Formation, Kansas
BB Bone bed locality in DPP, (Figure 1). Universal Transvers Mercator coordinates for these are given below as referenced in Eberth, in press:
BB 100 12; 462,600; 5,623.000
BB 54 12; 459,390; 5,629,207
P88.81.3 12; 427,000; 5,662,640
BB 43 12; 465,960; 5,622,340
Topographic Map of Dinosaur Provincial Park and Area Range 10,11,12. West of 4th meridian. Alberta Recreation and Parks. A.S. Project No. 79-395. Scale 1:10,000

Table 2. Hadrosaur femora size series (Judith River Formation). Samples are unique as they were obtained as a powder. This precluded mechanical cleaning prior to dialysis.

Sample Code	Length (mm)
HAD-F-1	765
HAD-F-2	807
HAD-F-3	960
HAD-F-4	970
HAD-F-5	977
HAD-F-6	990
HAD-F-7	1030
HAD-F-8	1035
HAD-F-9	1050
HAD-F-10	1066
HAD-F-11	1097
HAD-F-12	1170

Table 3. Samples of flora and sediments.

Specimen	Sample code	Collection Location*	Description**
Taxid	TAX-V-1	BPF	sequoia
Thuja	THU-V-1	BPF	cypress
Sediment 1	SED-TOF-1	BB 102	TOF
Sediment 1	SED-HMW-1	BB 102	HMW
Sediment 2	SED-TOF-2	BB 54	TOF
Sediment 2	SED-HMW-2	BB 54	HMW
Sediment 3	SED-TOF-3	BB 43	TOF
Sediment 3	SED-HMW-3	BB 43	HMW
Sediment 4	SED-TOF-4	BB 100	TOF
Sediment 4	SED-HMW-4	BB 100	HMW
Sediment 5	SED-TOF-5	BB 104	TOF
Sediment 5	SED-HMW-5	BB 104	HMW
Sediment 6	SED-HMW-6	TB	HMW

* Abbreviations for Collection Locations as given in Table 1 with the addition:
TB = Sediment associated with tyrannosaurid bone: TYR-B-1
Universal Transverse Mercator coordinates for sites not listed in Table 1:
BB 102 12; 455,610; 6,628,810
BB 104 12; 463,800; 5,622,250
The map is Topographic Map of Dinosaur Provincial Park and Area. See Table 1 for further details.

** HMW = high molecular weight organic fraction
TOF = total organic fraction

Table 4. Organic fractions isolated from modern bones and teeth and from Pleistocene and Cretaceous fossil bones and teeth: yields (percent of dry bone) and carbon to nitrogen elemental ratios.

Fraction	Yield (%)	C/N	Reference
Modern Collagen	22-27	2.7-3.6	4,5
Fossil Collagen	<1-28	2.9-3.6	2,3,9
Modern NCP*	3	4.2	1,6,7
Fossil NCP	nr/	4.2-4.8	8
Aggregates**	6-47	4.0-40	2
Fossil HMW//	<1-10	1.5-16.6	10
Hadrosaur HMW¥	1-13	11.1-48.0	10

* NCP noncollagen protein
** organic matter bound within aggregates
/ nr = not reported
// high molecular weight material isolated from all Late Cretaceous vertebrate fossils except those of the hadrosaur femora size series
¥ high molecular weight material isolated from bones of hadrosaur femora size series. Mechanical cleaning was not possible as these samples were obtained as a powder.

References:

1 DeNiro, 1985
2 DeNiro and Weiner, 1988
3 Dungworth et al., 1974
4 Hassan and Hare, 1978
5 Hare, 1980
6 Linde et al., 1984
7 Masters, 1987
8 Matter and Miller, 1972
9 Nelson et al., 1986
10 this study

Table 5. Elemental analysis and yield of high molecular weight material isolated from fossils of Late Cretaceous vertebrates, fossil plants, and sediments.

	Percent Nitrogen	Percent Carbon	C/N	Yield (%)
Aquatic Fish				
AMI-B-1	2.0	6.5	3.3	6.8
TEL-B-1	2.4	10.8	4.5	4.7
LEP-B-1	3.0	15.0	5.1	3
MYL-T-1	3.6	19.2	5.3	0.2
PAR-T-1	3.0	22.1	7.4	7
PAT-B-1	2.0	21.8	10.7	6.1
PTS-T-1	1.2	17.8	15.1	4.1
STU-T-1	0.6	1.4	2.4	5.2
Aquatic Reptiles				
ASP-B-2	0.7	3.5	5.0	7.3
CHA-B-1	2.4	7.6	3.2	3.4
CHA-T-1	nd[f]	nd	nd	nd
PLE-B-1	0.9	9.5	10.6	0.7
SCA-B-1	1.6	8.8	5.5	9.6
CRO-T-1	1.4	14.3	10.5	3.1
CRO-T-2	0.8	9.7	12.7	4.2
CRO-T-3	1.4	6.5	4.5	2.8
Mammal				
DIL-B-1	nd	nd	2.3	3.0
Terrestrial Vertebrates				
DRO-B-1	0.8	5.1	6.1	3.7
ORN-B-1	1.6	3.9	2.4	5.3
ORN-B-2	1.0	9.6	10.1	5.6
PAL-B-1	nd	nd	3.6	1.2
STE-B-1	1.2	6.5	5.5	4.4
CER-B-1	0.3	2.1	8.3	8.8
CER-B-2	2.7	4.6	1.7	6.3
CER-B-3	nd	nd	4.2	2.3
CER-T-1	nd	nd	nd	0.9
CER-T-2	0.8	13.5	16.6	5.1
CER-T-3	1.0	11.9	12.3	3.4
CER-T-4*	0.6	9.4	14.8	4.5
CER-T-4*	0.8	11.2	14.8	nd
CER-T-5	nd	nd	nd	3.3

Table 5 (cont.)

	Percent Nitrogen	Percent Carbon	C/N	Yield
HAD-B-1	5.1	10.9	2.1	3.2
HAD-T-1	0.6	8.2	13.0	5.4
HAD-T-2	0.9	6.9	8.1	6.7
HAD-T-3	nd	nd	7.2	7.6
HAD-T-4	1.7	2.6	1.5	2.0
NOD-T-1	0.7	7.4	11.2	4.7
NOD-T-2	nd	nd	nd	2.5
PAN-T-1	1.5	11.7	7.9	0.8
TYR-B-1	0.8	2.5	3.2	7.9
TYR-T-1	nd	nd	nd	1.0
TYR-T-2	0.7	7.6	11.0	5.1
TYR-T-3	2.0	18.0	9.3	1.6
Hadrosaur Femora				
HAD-F-1	0.4	8.4	27.1	7.7
HAD-F-2	0.4	7.7	23.5	6.0
HAD-F-3	0.5	9.5	24.8	9.3
HAD-F-4	0.3	9.8	33.8	3.7
HAD-F-5	0.8	17.2	24.0	0.8
HAD-F-6	0.4	4.4	12.9	12.9
HAD-F-7	0.7	13.1	22.7	3.7
HAD-F-8	0.2	6.3	40.1	8.1
HAD-F-9	0.2	5.7	28.5	3.5
HAD-F-10	1.0	16.2	18.5	2.6
HAD-F-11	0.7	7.0	11.1	2.7
HAD-F-12	0.2	6.0	48.0	5.9
Marine Vertebrates				
MOS-T-1	nd	nd	5.5	2.8
SHA-T-1	nd	nd	nd	1.3
MOS-B-1	nd	nd	nd	4.3
MOS-T-2	nd	nd	3.4	4.8

ƒ nd = not determined
* replicate values

Table 6. Replicate GCMS analyses of amino acid enantiomers. *STD 1 and STD 2 are replicate derivatizations of the standard amino acid mixture. STD 1-1 and STD 1-2 are replicate analyses of STD-1

	D-Ala	L-Ala	D/L Ala	D-Thr	L-Thr	D/L Thr
STD* 1-1	834321	987850	0.845	414695	583865	0.710
STD 1-2	911006	1066717	0.854	309139	701147	0.441
STD 2-1	854103	1018049	0.839	306117	762004	0.402
AVERAGE	866476	1024205	0.846	343317	673984	0.518
SD*	32506	32490	0.008	50486	65378	0.168
CV*	0.03	0.03	0.009	0.15	0.1	0.325

	D-Val	L-Val	D/L Val	D-Ile	L-Ile	D/L Ile
STD 1-1	745891	711349	1.049	540905	575398	0.950
STD 1-2	770788	965361	0.798	608028	633306	0.960
STD 2-1	949086	949086	1.000	617130	627372	0.984
AVERAGE	759561	875265	0.949	588687	612025	0.965
SD	10309	116096	0.133	33991	26012	0.017
CV	0.01	0.13	0.140	0.06	0.04	0.018

	D-Leu	L-Leu	D/L Leu	D-Pro	L-Pro	D/L Pro
STD 1-1	967590	847115	1.142	1091847	1164519	0.938
STD 1-2	1131095	968603	1.168	985142	1302379	0.756
STD 2-1	1053308	994862	1.059	1159237	1448154	0.800
AVERAGE	1050664	936860	1.123	1078742	1305017	0.831
SD	66777	64358	0.057	71676	115808	0.094
CV	0.06	0.07	0.051	0.07	0.09	0.113

Table 6 (cont.)

		D-Asp	L-Asp	D/L Asp	D-Met	L-Met	D/L Met
STD	1-1	947563	972979	0.974	704313	715874	0.984
STD	1-2	936631	963597	0.972	785796	759974	1.034
STD	2-1	1085904	1101184	0.986	793532	843495	0.941
AVERAGE		990032	1012586	0.977	761213	773114	0.986
SD		67938	62764	0.008	40358	52923	0.047
CV		0.07	0.06	0.008	0.05	0.07	0.047

		D-Glu	L-Glu	D/L Glu	D-Phe	L-Phe	D/L Phe
STD	1-1	662615	1086244	0.610	661515	1113982	0.59382
STD	1-2	707125	1170570	0.604	707125	1148897	0.61548
STD	2-1	64405	1357392	0.474	911055	1180384	0.77182
AVERAGE		808048	1204735	0.561	759898	1147754	0.674
SD		175145	113301	0.074	108493	27121	0.09
CV		0.22	0.09	0.13	0.14	0.02	0.13

		Gly	Hypro	Hylys	Lys
STD	1-1	468155	1089893	294215	622259
STD	1-2	452676	1095672	252608	673202
STD	2-1	434296	1102502	326516	866643
AVERAGE		451709	1096022	291113	720701
SD		13840	5154	30252	105271
CV		0.03	0.01	0.10	0.15

*SD is one standard deviation about the mean.
¥CV is the coefficient of variation = SD/AVERAGE

Table 7. Enantiomer ratios of HMW material isolated from samples of Late Cretaceous vertebrate fossils.

Sample Number	D/L Ala	D/L Thr	D/L Val	D/L Ile	D/L Leu
Aquatic Vertebrates					
AMI-B-1	0.182				0.051
TEL-B-1	0.229	0.045			0.089
LEP-S-1					0.077
PAR-T-1	0.190		0.030		0.155
PAT-B-1	0.201				0.074
CHA-B-1	0.170				0.039
CHA-T-1	0.095	0.035			0.227
SCA-B-1					
CRO-T-1	0.121	0.010		0.064	
CRO-T-2	0.145				
CRO-T-3*	0.225	0.068	0.384		
Terrestrial Vertebrates					
ORN-B-1	0.212	0.054			
ORN-B-2	0.030			0.286	
STE-B-1	0.098				0.13
CER-B-2	0.097				0.114
CER-B-2*	0.149				0.09
CER-T-1	0.175				0.074
CER-T-2*	0.112				
CER-T-2	0.159	0.064			0.043
CER-T-6	0.181		0.126		0.119
HAD-B-1*	0.086				
HAD-T-2*	0.227				
HAD-T-3	0.051				0.12
HAD-T-4	0.087				0.083
TYR-B-1*	0.102				
TYR-T-1	0.127	0.181			0.140
TYR-T-2*	0.206				
TYR-T-2[v]	0.107				0.043
TYR-T-2[v]	0.109			0.176	0.022
Observations	26	6	3	2	15
Minimum	0.030	0.010	0.030	0.064	0.039
Maximum	0.229	0.181	0.384	0.286	0.227
Mean	0.159	0.065	0.180	0.175	0.101
SD	0.071	0.055	0.183	0.110	0.104

Table 7.(cont.)

Sample Number	D/L Ser	D/L Pro	D/L Asp	D/L Glu	D/L Phe
AMI-B-1					
TEL-B-1			0.210	0.352	0.161
LEP-S-1					
PAR-T-1		0.163			
PAT-B-1					
CHA-B-1	0.263				
CHA-T-1		0.165	0.112		0.152
SCA-B-1					
CRO-T-1		0.175	0.175		
CRO-T-2			0.037	0.027	
CRO-T-3					
ORN-B-1					
ORN-B-2	0.314				
STE-B-1					
CER-B-2					
CER-B-2			0.05	0.231	0.181
CER-T-1			0.026	0.190	
CER-T-2*			0.016	0.031	
CER-T-2					
CER-T-6					
HAD-B-1			0.054	0.115	
HAD-T-2			0.102	0.067	
HAD-T-3					
HAD-T-4					0.044
TYR-B-1			0.068	0.079	
TYR-T-1		0.097	0.140		
TYR-T-2			0.054	0.039	
TYR-T-2¥					
TYR-T-2¥					
Observations	2	4	12	9	4
Minimum	0.263	0.097	0.016	0.027	0.044
Maximum	0.314	0.175	0.210	0.352	0.181
Mean	0.289	0.150	0.087	0.126	0.135
SD	0.036	0.035	0.062	0.111	0.062

* Samples derivatized as N-TFA isopropyl esters at the University of Oklahoma
¥ Replicate analyses

Table 8. Enantiomer ratios of the total organic fraction (TOF) and high molecular weight (HMW) component of samples of Late Cretaceous vertebrate fossils.

SAMPLE CODE		D/L Ala	D/L Leu	D/L Asp	D/L Glu	D/L Phe
CER-B-2	TOF	0.104	0.125	0.126	0.627	0.315
CER-B-2	HMW	0.149	0.090	0.050	0.231	0.181
CER-T-4	TOF	0.101	0.118	0.129	nd	0.260
CER-T-4	HMW	nd*	nd	0.026	0.190	nd
HAD-B-1	TOF	0.112	0.142	0.130	0.755	0.303
HAD-B-1	HMW	0.086	nd	0.054	0.115	nd

*nd = not determined

Table 9. Values of the D/L of Ala the total organic fraction (TOF) of sediments. Replicate value indicated in the parenthesis.

SAMPLE CODE	D/L Ala
Sediments: TOF	
SED-TOF-1	0.228
SED-TOF-2	0.155 (.154)
SED-TOF-4	0.154
Mean	0.179 ± 0.04

Table 10. Comparison of enantiomer ratios of HMW material from a tyrannosaur bone and associated sediment.

SAMPLE CODE	D/L Ala	D/L Asp	D/L Phe
TYR-B-1	0.102	0.068	0.079
SED-HMW-6*	0.186	0.117	0.253

* Sample derivatized as a N-TFA isopropyl ester at the University of Oklahoma

Table 11 Characterization of the high molecular weight component of fossils of Late Cretaceous vertebrates in terms of amino acid concentration (AA CONC), percent amino acid weight (% AWT), percentage of sample weight contributed by amino acid carbon and nitrogen (%AC and %AN, respectively), percent of total nitrogen and carbon contributed by amino acids (%NA and %CA, respectively).

	Amino Acid Concentration ($\mu M \cdot g^{-1}$)	%AWT	%AC	%AN	%NA	%CA
AMI-B-1	16.7	0.2	0.1	0.02	1.02	1.08
TEL-B-1	29.0	0.4	0.2	0.07	2.90	1.48
LEP-B-1	2.4	<0.1[f]	<0.1	0.01	0.03	0.01
PAR-T-1	22.0	0.3	0.09	0.04	1.34	0.41
PAT-B-1	4.8	0.1	0.02	0.01	0.49	0.09
STU-T-1	10.9	0.1	0.05	0.02	3.50	3.39
ASP-B-2	38.2	0.4	0.18	0.05	7.25	5.21
CHA-B-1	26.1	0.3	0.13	0.04	1.67	1.71
PLE-B-1	12.4	0.2	0.07	0.02	2.25	0.74
SCA-B-1	10.4	0.2	0.07	0.04	2.48	0.80
CRO-T-1	27.4	0.3	0.13	0.04	2.94	0.91
CRO-T-2	9.4	0.1	0.04	0.01	1.30	0.41
CRO-T-3	3.1	<0.1	0.01	0.00	0.39	0.15
DRO-B-1	15.7	0.2	0.09	0.03	3.61	1.78
ORN-B-1	25.0	0.3	0.14	0.04	2.43	3.62
ORN-B-2	32.8	0.4	0.16	0.05	5.26	1.67
STE-B-1	9.4	0.1	0.05	0.01	0.86	0.73
CER-B-1	6.1	0.1	0.03	0.01	3.85	1.45
CER-B-2	5.2	0.5	0.21	0.07	2.59	4.62
CER-T-1	16.4	0.2	0.07	0.02	nd*	nd
CER-T-2	6.9	0.1	0.03	0.01	1.23	0.23
CER-T-3	19.9	0.2	0.09	0.03	3.13	0.79
CER-T-4	4.2	0.1	0.02	0.01	1.59	0.19
HAD-B-1	3.1	<0.1	0.02	<0.01	0.08	0.18
HAD-T-1	5.0	0.1	0.02	0.01	1.58	0.24
HAD-T-2	3.4	<0.1	0.02	<0.01	0.11	0.29
HAD-T-4	26.3	0.3	0.12	0.04	2.38	4.65
NOD-T-1	5.1	0.06	0.02	0.01	1.52	0.27
NOD-T-2	3.1	0.03	0.01	<0.01	nd	nd
PAN-T-1	11.3	0.13	0.05	0.02	1.35	0.43
TYR-B-1	18.2	0.18	0.08	0.02	2.63	3.27
TYR-T-1	32.2	0.36	0.15	0.05	nd	nd
TYR-T-2	1.5	0.02	0.01	<0.01	0.14	0.13

*nd = not determined [f] <0.01 = less than 0.01

Table 12. Published data for amino acid concentrations of Recent to Jurassic fossils ($\mu M \cdot g^{-1}$ of fossil).

Amino Acid Concentration ($\mu M \cdot g^{-1}$)	Age of Fossil	Reference
2 to 2300	Recent	Hare, 1980
3 to 1830	Pleistocene	Dungworth et al., 1974
11 to 32	Pleistocene	Wycoff et al., 1964
4.6	Pliocene	Dungworth et al., 1974
3.5	Miocene	Dungworth et al., 1974
0.5 to 1.7*	Cretaceous	Matter and Miller, 1972
0.1 to 0.4*	Cretaceous	Miller and Wycoff, 1968
<0.1 to 1.4	Cretaceous	This study
0.1 to 0.2*	Jurassic	Miller and Wycoff, 1968

* Original data in $mg \cdot g^{-1}$ or $\mu g \cdot g^{-1}$, these values were calculated based on the molecular weight of individual amino acids

Table 13. Replicate analyses of amino acid compositions for two ceratopsid teeth and one hadrosaur tooth.

Amino Acid Concentration ($\mu M \cdot g^{-1}$)

	CER-T-1	CER-T-1	CER-T-2	CER-T-2	HAD-T-1	HAD-T-1
Asp	1.9	1.8	0.9	0.7	0.7	1.0
Thr	0.9	1.6	0.6	1.0	0.4	0.4
Ser	3.1	3.4	0.7	1.0	0.9	1.2
Glu	2.8	2.9	1.0	1.0	0.6	0.9
Gly	3.7	3.5	1.2	1.4	1.0	1.4
Ala	1.3	1.2	0.7	0.7	0.5	0.7
Val	1.3	1.3	0.9	1.0	ndt*	ndt
Met	ndt	ndt	ndt	ndt	ndt	ndt
Ile	0.3	0.3	0.3	0.3	0.1	<0.1
Leu	0.5	0.4	0.3	0.3	<0.1	<0.1
Tyr	ndt	ndt	nd	ndt	ndt	ndt
Phe	ndt	ndt	nd	ndt	ndt	ndt
His	nd¥	ndt	ndt	ndt	ndt	ndt
Lys	<0.1f	<0.1	<0.1	<0.1	nd	nd
Arg	0.1	0.1	<0.1	<0.1	nd	nd
TOTAL	15.4	16.4	6.4	7.4	4.2	5.6

Amino Acid Composition (mole percent)

	CER-T-1	CER-T-1	CER-T-2	CER-T-2	HAD-T-1	HAD-T-1
Asp	11.9	10.9	14.1	9.7	17.8	17.9
Thr	5.8	9.8	8.9	13.2	9.3	6.2
Ser	19.8	20.9	11.1	13.1	20.9	20.7
Glu	17.6	17.5	15.1	14.2	15.4	16.7
Gly	23.7	21.2	18.0	18.8	23.0	25.2
Ala	8.3	7.5	10.3	9.4	12.2	12.4
Val	8.2	8.1	13.6	14.0	ndt	ndt
Met	ndt	ndt	nd	nd	ndt	ndt
Ile	1.7	1.7	4.1	3.7	1.2	0.2
Leu	3.1	2.5	4.7	4.0	0.2	0.2
Tyr	ndt	ndt	nd	nd	ndt	ndt
Phe	ndt	ndt	nd	nd	ndt	ndt

* ndt = not detected ¥ nd = not determined
f <0.1 = less than 0.1

Table 14. Average difference between replicates analyses of amino acids concentration. (Data for replicates presented in Table 13).

Amino Acid	Average	Four Standard Deviations	Difference Required to be Significant
Asp	1.8	8.6	10.4
Thr	3.8	2.4	7.0
Ser	1.0	3.8	4.8
Glu	0.5	3.0	3.5
Gly	1.8	3.6	5.4
Ala	0.7	1.4	2.1
Val	0.2	0.8	1.0
Ile	0.5	2.0	2.5
Leu	0.5	1.6	2.1

Table 15. Amino acid compositions (mole percent, %) of modern collagens, high molecular weight (HMW) material, and non-collagen proteins.

	Collagen					HMW
	Ox Bone	Bison Bone	Cod Bone	Bovine Bone	Bovine Tooth	Bovine Bone
Asp	4.3	4.6	5.2	5.0	5.8	6.7
Thr	1.9	2.0	2.4	1.9	1.7	2.9
Ser	3.5	3.5	7.0	3.5	3.6	4.8
Glu	6.4	7.7	7.2	7.8	7.3	8.4
Gly	31.7	32.3	34.9	33.0	33.0	21.7
Ala	10.8	11.3	10.7	11.2	10.1	9.3
Val	2.4	2.3	1.8	2.1	1.9	4.2
Met	0.5	0.6	1.4	0.4	1.5	0.8
Ile	1.3	1.2	1.2	1.1	1.4	2.0
Leu	3.0	2.8	2.3	2.8	3.2	5.5
Tyr	0.7	0.5	0.3	0.4	0.4	1.2
Phe	1.9	1.5	0.8	1.4	1.8	2.4
His	0.6	0.5	0.7	0.4	0.8	1.6
Lys	3.0	2.7	2.3	2.5	2.4	3.7
Arg	5.0	4.9	4.9	5.3	5.2	3.9
Pro	11.8	11.6	9.9	10.9	11.1	10.8
Hypro	10.3	9.4	5.9	6.3	7.7	9.6
Hylys	0.8	0.5	0.8	0.4	1.1	0.8
REFERENCE	6	6	5	1	6	7

Table 15. (cont.)

	Phosphophoryn Bovine Tooth	Proteoglycan Bovine Bone	Osteocalcin Bovine bone
Asp	33.5	16.2	14.2
Thr	1.3	8.7	nd*
Ser	43.9	9.7	nd
Glu	2.7	19.4	6.1
Gly	3.5	14.0	8.1
Ala	1.4	3.8	8.1
Val	0.9	3.1	4.1
Met	0.4	<0.1[f]	nd
Ile	nd	1.9	20.2
Leu	1.3	3.4	10.2
Tyr	0.5	1.9	8.0
Phe	0.5	1.6	4.0
His	0.7	2	4.0
Lys	5.3	3.4	2.0
Arg	0.9	4.2	6.0
Pro	1.8	6.3	12.1
Hypro	nd	nd	2.0
Hylys	nd	nd	nd
Gla¥	nd	nd	6.0
REFERENCE	4	2	3

* nd = not determined *f* <0.1 = <0.1
¥ Gla = γ-Carboxyglutamic acid

References:
1 Hare, 1980
2 Herring, 1968
3 Price et al, 1976
4 Stetler-Stevenson and Veis, 1983
5 Tristram and Smith, 1963
6 Wycoff, 1972
7 This study

Table 16. Amino acid concentrations ($\mu M \cdot g^{-1}$) of high molecular weight material isolated form fossils of Late Cretaceous aquatic vertebrates.

	AMI-B-1	TEL-B-1	LEP-S-1	PAR-B-1	PAT-B-1
Asp	1.5	2.4	0.1	3.3	0.6
Thr	0.3	1.4	0.4	1.6	0.3
Ser	0.5	1.7	<0.1	2.0	0.5
Glu	2.1	4.1	0.4	4.2	0.8
Gly	3.5	2.6	0.7	3.1	1.4
Ala	2.9	2.9	0.5	2.7	0.8
Val	2.6	0.6	0.3	0.7	0.1
Met	2.2	ndt*	ndt	0.3	0.1
Ile	0.2	0.7	<0.1	0.6	0.1
Leu	0.9	1.4	<0.1	1.1	0.1
Tyr	<0.1[f]	ndt	ndt	ndt	<0.1
Phe	<0.1	ndt	ndt	ndt	<0.1
His	nd	6.5	nd	ndt	nd
Lys	<0.1	3.2	nd	2.4	nd
Arg	0.2	1.0	nd	nd	nd
Pro	ndt	ndt	nd	0.1	ndt
Hypro	ndt	0.5	nd	<0.1	ndt
Hylys	ndt	<0.1	nd	<0.1	ndt
TOTAL	16.7	29.0	2.4	22.0	4.8
% AC**	0.02	0.07	0.01	0.04	0.01
% AN**	0.08	0.16	0.01	0.09	0.02
% AWT**	0.19	0.37	0.03	0.25	0.05

Table 16 (cont.)

	STU-T-1	ASP-B-2	CHA-B-1	PLE-B-1	SCA-B-1
Asp	1.2	4.8	1.1	1.3	0.6
Thr	0.4	2.8	<0.1	0.4	ndt
Ser	1.1	3.2	<0.1	1.6	ndt
Glu	1.6	6.7	10.1	1.9	0.5
Gly	1.7	5.8	6.8	2.1	0.8
Ala	1.5	6.0	3.0	0.7	0.4
Val	1.6	3.6	2.5	1.4	nd
Met	1.3	0.4	0.7	1.3	ndt
Ile	0.2	1.7	0.8	0.7	ndt
Leu	0.2	3.4	1.2	ndt	ndt
Tyr	<0.1	<0.1	ndt	0.4	ndt
Phe	<0.1	0.1	ndt	0.8	nd
His	<0.1	nd	nd	nd	nd
Lys	<0.1	nd	nd	nd	3.6
Arg	<0.1	<0.1	nd	nd	4.5
Pro	nd	ndt	nd	0.1	nd
Hypro	nd	ndt	nd	<0.1	nd
Hylys	nd	ndt	nd	<0.1	nd
TOTAL	10.9	38.2	26.1	12.5	10.4
% AN	0.02	0.05	0.04	0.02	0.04
% AC	0.05	0.18	0.13	0.07	0.07
% AWT	0.13	0.44	0.31	0.15	0.16

Table 16 (cont.)

	CRO-T-1	CRO-T-2	CRO-T-3
Asp	2.1	1.0	0.7
Thr	4.9	0.6	nd
Ser	1.1	0.6	0.2
Glu	4.2	2.5	0.5
Gly	3.9	2.3	0.9
Ala	3.5	1.2	0.3
Val	1.7	1.3	0.3
Met	3.3	ndt	0.1
Ile	<0.1	ndt	<0.1
Leu	0.2	ndt	0.1
Tyr	0.5	ndt	nd
Phe	0.1	ndt	nd
His	<0.1	nd	nd
Lys	nd	nd	0.1
Arg	nd	nd	nd
Pro	0.7	nd	nd
Hypro	0.2	nd	0.1
Hylys	ndt	nd	<0.1
TOTAL	26.4	9.4	3.1
% AN	0.04	0.01	<0.01¢
% AC	0.13	0.04	0.01
% AWT	0.30	0.11	0.04

* ndt = not detected
¥ nd = not determined
ƒ <0.1 = less than 0.1
¢ <0.01 = less than 0.01
** % AC = Percent amino acid carbon
% AN = Percent amino acid carbon
% AWT = Percent of weight that contributed by amino acids

Table 17. Amino acid concentrations ($\mu m \cdot g^{-1}$) of high molecular weight material isolated from fossils of Late Cretaceous terrestrial and marine vertebrates. Abbreviations are defined in Table 16 unless otherwise noted.

	DRO-B-1	ORN-B-1	ORN-B-2	STE-B-1	CER-B-1	CER-B-2
Asp	1.7	1.2	4.1	0.5	0.5	6.0
Thr	0.5	0.5	2.3	1.7	0.3	2.5
Ser	1.3	0.7	2.3	2.8	0.7	3.1
Glu	2.1	18.2	5.7	0.4	0.8	6.8
Gly	1.7	1.8	4.0	1.2	0.7	11.9
Ala	0.7	1.1	5.0	0.2	0.5	3.3
Val	nd	0.8	3.3	0.4	0.3	0.4
Met	nd	<0.1	0.7	0.2	<0.1	1.6
Ile	4.2	0.1	1.3	0.9	0.3	2.2
Leu	0.9	0.1	2.4	1.1	0.6	<0.1
Tyr	<0.1	<0.1	<0.1	nd	0.1	0.9
Phe	<0.1	<0.1	0.1	<0.1	0.1	1.7
His	nd	nd	nd	nd	nd	nd
Lys	0.8	0.6	1.0	0.1	0.3	2.3
Arg	1.7	nd	0.5	nd	1.3	0.4
Pro	nd	nd	nd	nd	ndt	nd
Hypro	nd	nd	nd	nd	0.1	nd
Hylys	nd	nd	nd	nd	ndt	nd
TOTAL	15.7	25.0	32.8	9.4	6.6	43.1
% AN	0.03	0.04	0.05	0.01	0.01	0.07
% AC	0.09	0.14	0.16	0.05	0.03	0.21
% AWT	0.20	0.34	0.39	0.11	0.06	0.51

Table 17 (cont.)

	CER-B-3	CER-T-1*	CER-T-2*	CER-T-3	CER-T-4
Asp	<0.1	1.8	0.8	2.1	0.6
Thr	nd	1.3	0.8	1.8	0.2
Ser	0.1	3.2	0.8	2.9	0.5
Glu	<0.1	2.8	1.0	3.2	0.8
Gly	0.3	3.8	1.3	4.0	1.0
Ala	0.1	1.3	0.7	1.6	0.3
Val	<0.1	1.3	1.0	2.2	0.3
Met	ndt	ndt	ndt	nd	<0.1
Ile	<0.1	0.3	0.3	0.4	nd
Leu	<0.1	0.5	0.3	0.5	0.1
Tyr	ndt	ndt	ndt	<0.1	<0.1
Phe	<0.1	ndt	ndt	<0.1	<0.1
His	nd	nd	nd	nd	nd
Lys	<0.1	<0.1	<0.1	1.1	0.5
Arg	nd	0.1	<0.1	nd	nd
Pro	nd	ndt	ndt	nd	nd
Hypro	nd	0.2	ndt	nd	nd
Hylys	nd	ndt	ndt	nd	nd
TOTAL	0.7	16.4	6.9	19.9	4.2
% AN	0.02	0.02	0.01	0.03	0.01
% AC	0.03	0.07	0.03	0.10	0.02
% AWT	0.01	0.19	0.08	0.23	0.05

Table 17 (cont.)

	CER-T-5	HAD-B-1	HAD-T-1*	HAD-T-2	HAD-T-3
Asp	1.5	0.3	0.9	0.4	1.1
Thr	0.8	0.1	0.4	0.1	0.6
Ser	1.0	0.4	1.0	0.3	1.0
Glu	2.4	0.5	0.8	0.6	1.5
Gly	2.0	0.5	1.2	0.9	1.3
Ala	2.5	0.4	0.6	0.3	0.9
Val	1.3	0.1	ndt	0.3	0.3
Met	0.1	<0.1	ndt	nd	nd
Ile	<0.1	0.2	<0.1	0.5	0.3
Leu	1.0	0.2	<0.1	0.1	0.4
Tyr	<0.1	0.1	ndt	<0.1	ndt
Phe	<0.1	0.3	ndt	nd	ndt
His	nd	nd	nd	nd	nd
Lys	0.4	0.1	nd	nd	nd
Arg	nd	0.1	nd	nd	nd
Pro	nd	ndt	nd	nd	nd
Hypro	nd	<0.1	nd	nd	nd
Hylys	nd	ndt	nd	nd	nd
TOTAL	12.9	3.1	4.9	3.4	7.3
% AN	0.02	<0.01	0.01	<0.01	0.01
% AC	0.06	0.02	0.02	0.02	0.03
% AWT	0.15	0.04	0.05	0.04	0.08

Table 17 (cont.)

	HAD-T-4	NOD-T-1	NOD-T-2	PAN-T-1	TYR-B-1
Asp	2.9	0.7	0.5	1.5	0.7
Thr	1.0	0.3	0.2	0.5	2.3
Ser	3.9	0.6	0.2	1.8	3.0
Glu	5.5	1.0	0.8	2.6	2.1
Gly	5.8	1.0	0.9	2.6	3.5
Ala	2.2	0.6	0.4	0.9	2.3
Val	3.4	0.3	0.1	nd	0.9
Met	<0.1	<0.1	<0.1	<0.1	1.0
Ile	0.8	0.2	<0.1	0.3	0.4
Leu	0.8	0.2	0.1	1.1	0.7
Tyr	<0.1	<0.1	ndt	<0.1	0.3
Phe	<0.1	<0.1	ndt	0.1	0.3
His	nd	nd	nd	nd	nd
Lys	nd	0.1	nd	0.1	1.0
Arg	nd	nd	nd	nd	0.6
Pro	nd	nd	nd	nd	ndt
Hypro	nd	nd	nd	nd	0.1
Hylys	nd	nd	nd	nd	ndt
TOTAL	26.3	5.1	3.1	11.3	19.1
% AN	0.04	0.01	<0.01	0.02	0.02
% AC	0.12	0.02	0.01	0.05	0.08
% AWT	0.30	0.06	0.03	0.13	0.18

Table 17 (cont.)

	TYR-T-1	TYR-T-2	SHA-T-2	MOS-T-1
Asp	3.8	0.2	0.8	0.6
Thr	1.6	0.1	0.2	0.2
Ser	3.9	0.2	0.5	0.1
Glu	0.5	0.2	0.6	0.7
Gly	7.8	0.3	0.8	0.9
Ala	5.5	0.1	0.1	0.8
Val	3.9	0.1	0.4	0.5
Met	0.3	ndt	ndt	nd
Ile	1.0	0.1	nd	0.1
Leu	2.0	0.1	nd	0.1
Tyr	<0.1	<0.1	nd	nd
Phe	<0.1	<0.1	nd	nd
His	nd	0.1	nd	nd
Lys	nd	<0.1	nd	<0.1
Arg	nd	<0.1	nd	nd
Pro	nd	0.1	nd	nd
Hypro	1.0	nd	nd	nd
Hylys	0.9	nd	nd	nd
TOTAL	32.2	1.4	3.4	4.0
% AN	0.05	<0.01	<0.01	0.01
% AC	0.15	0.01	0.01	0.02
% AWT	0.36	0.02	0.04	0.04

* average values

Table 18. Amino acid composition (mole percent) of HMW material from fossils of Late Cretaceous aquatic vertebrates. Abbreviations are defined in Table 16 and 17.

	AMI-B-1	TEL-B-1	LEP-S-1	PAR-T-1	PAT-B-1
Asp	9.3	13.4	2.3	16.9	13.2
Thr	1.6	8.0	15.0	8.1	6.0
Ser	3.0	9.5	1.7	10.0	10.7
Glu	12.6	23.0	17.4	21.4	16.4
Gly	21.3	14.6	27.4	15.9	28.3
Ala	17.3	16.1	22.5	13.7	16.1
Val	15.5	3.4	12.3	3.5	2.9
Met	13.2	ndt	ndt	1.5	2.3
Ile	1.1	4.1	0.7	3.1	1.8
Leu	5.2	8.0	0.8	5.9	1.8
Tyr	<0.1	ndt	ndt	ndt	0.2
Phe	<0.1	ndt	ndt	ndt	0.2

	STU-T-1	ASP-B-1	CHA-B-1	PLE-B-1	SCA-B-1
Asp	11.0	12.5	4.3	10.1	26.4
Thr	4.0	7.4	0.1	3.4	nd
Ser	9.6	8.3	<0.1	13.1	ndt
Glu	15.0	17.5	38.6	14.9	22.3
Gly	16.0	15.0	26.0	17.2	35.7
Ala	13.5	15.6	11.5	5.4	15.6
Val	15.1	9.3	9.7	11.4	ndt
Met	11.6	1.0	2.5	10.1	ndt
Ile	2.1	4.4	2.9	5.3	ndt
Leu	1.9	8.8	4.4	ndt	ndt
Tyr	0.2	0.1	ndt	3.2	ndt
Phe	0.1	0.2	ndt	6.1	ndt

	CRO-T-1	CRO-T-2	CRO-T-3
Asp	8.4	10.9	21.2
Thr	19.3	10.1	0.1
Ser	4.3	15.1	7.3
Glu	16.5	17.0	16.6
Gly	15.3	20.5	28.7
Ala	13.8	11.6	9.3
Val	6.6	11.3	9.5
Met	12.8	ndt	1.8
Ile	<0.1	2.4	1.3
Leu	0.7	4.3	1.4
Tyr	2.0	ndt	ndt
Phe	0.2	ndt	ndt
Ile	<0.1	2.4	1.3
Leu	0.7	4.3	1.4
Tyr	2.0	ndt	ndt
Phe	0.2	ndt	ndt

Table 19 Amino acid composition (mole percent) of HMW material from fossils of Late Cretaceous terrestrial and marine vertebrates. Abbreviations are defined in Tables 16 and 17.

	DRO-B-1	ORN-B-1	ORN-B-2	STD-B-1	CER-B-1	CER-B-2
Asp	13.1	5.2	13.1	5.6	10.8	15.0
Thr	3.4	2.3	7.5	17.7	6.8	6.1
Ser	10.1	2.9	7.5	29.8	14.3	7.8
Glu	16.3	74.3	18.1	4.5	16.3	16.7
Gly	13.1	6.6	12.9	12.8	13.4	29.4
ALA	5.3	4.0	16.1	2.1	9.7	8.2
Val	nd	3.7	10.6	4.0	6.9	0.9
Met	<0.1	0.1	2.1	2.3	0.1	4.0
Ile	31.8	0.6	4.2	9.4	5.1	5.5
Leu	6.5	0.3	7.7	11.6	11.2	<0.1
Tyr	0.3	<0.1	<0.1	<0.1	2.4	2.2
Phe	0.1	0.1	0.2	0.1	3.0	4.3

	CER-B-3	CER-T-1*	CER-T-2*	CER-T-3	CER-T-4
Asp	6.2	11.4	11.9	10.5	15.4
Thr	nd	7.8	11.1	9.0	5.3
Ser	17.0	20.4	12.1	14.4	12.9
Glu	4.1	17.6	14.6	15.6	20.6
Gly	36.5	22.4	18.4	19.4	26.7
Ala	14.5	7.9	9.9	8.0	7.6
Val	6.1	8.2	13.8	18.6	8.4
Met	ndt	ndt	ndt	<0.1	0.2
Ile	5.7	1.7	3.9	1.8	0.1
Leu	5.7	2.8	4.3	2.6	2.6
Tyr	nd	ndt	ndt	nd	0.2
Phe	4.2	ndt	ndt	nd	0.2

	CER-T-5	HAD-B-1	HAD-T-1*	HAD-T-2	HAD-T-3
Asp	11.6	9.8	17.9	10.7	14.5
Thr	6.4	4.5	7.8	2.5	7.8
Ser	7.8	12.4	20.9	10.1	14.2
Glu	18.8	15.6	16.1	15.9	20.5
Gly	15.8	16.0	24.2	25.6	17.8
Ala	19.8	13.0	12.4	7.6	11.7
Val	10.4	2.7	ndt	8.5	4.1
Met	0.6	0.3	ndt	nd	nd
Ile	0.1	6.5	0.7	15.6	4.0
Leu	0.3	8.3	0.2	3.3	5.5
Tyr	0.1	2.1	ndt	0.2	ndt
Phe	0.3	8.8	ndt	ndt	ndt

Table 19 (cont.)

	HAD-T-4	NOD-T-1	NOD-T-2	PAN-T-1	TYR-B-1
Asp	10.9	14.1	17.1	13.4	4.1
Thr	3.8	6.7	5.0	4.1	12.9
Ser	14.7	11.3	7.2	15.7	17.2
Glu	20.9	19.2	25.0	23.2	12.5
Gly	22.3	20.7	27.5	23.2	20.1
Ala	8.3	12.9	14.1	8.1	13.2
Val	12.9	5.6	1.8	nd	5.1
Met	<0.1	0.4	0.2	<0.1	5.7
Ile	3.1	4.0	0.7	2.2	2.3
Leu	3.1	4.9	1.5	9.6	3.9
Tyr	0.1	0.1	ndt	0.2	2.0
Phe	0.1	0.1	ndt	0.6	1.1

	TYR-T-1	TYR-T-2	SHA-T-2	MOS-T-1
Asp	12.6	13.6	22.7	14.5
Thr	5.2	5.2	5.1	3.7
Ser	12.9	15.2	14.6	3.2
Glu	1.8	15.1	18.1	17.9
Gly	25.6	23.4	23.9	22.2
Ala	18.1	7.0	2.6	19.9
Val	12.8	4.3	13.0	13.4
Met	1.0	0.2	ndt	ndt
Ile	3.3	4.4	nd	3.6
Leu	6.7	9.7	nd	1.8
Tyr	<0.1	1.2	nd	0.1
Phe	<0.1	0.9	nd	0.1

* average value

Table 20. Yield of total amino acids from TOF and corresponding HMW material.

	Concentration of Total Amino Acids $\mu M \cdot g^{-1}$ bone		
	TYR-T-1	HAD-B-1	CER-T-2
TOF	5.90	1.34	10.08
HMW	0.32	0.10	0.35

Table 21. Amino acid concentrations as $\mu M \cdot g^{-1}$ bone for the total organic fraction (TOF) and mole percent (based on percent of bone) for TOF and high molecular weight (HMW) material of fossils of Late Cretaceous vertebrates. Abbreviations are defined in Tables 16 and 17.

	AMINO ACID CONCENTRATION ($\mu M \cdot g^{-1}$)		
	TYR-T-1	HAD-B-1	CER-T-2
Asp	1.1	0.1	1.3
Thr	0.2	<0.1	1.5
Ser	1.1	0.3	1.2
Glu	0.3	0.1	1.8
Gly	0.4	0.1	1.5
Ala	0.2	0.5	1.0
Val	1.9	<0.1	1.4
Met	<0.1	<0.1	0.5
Ile	<0.1	<0.1	0.8
Leu	<0.1	<0.1	<0.1
Tyr	nd	<0.1	<0.1
Phe	nd	<0.1	nd
His	nd	nd	0.1
Lys	0.8	0.2	nd
Arg	nd	<0.1	0.0
TOTAL	5.9	1.3	10.1
% Amino Acid N	0.01	<0.01	0.01
% Amino Acid C	0.03	0.01	0.05
% Amino Acid Weight	0.07	0.01	0.12

	PERCENT AMINO ACID					
	TYR-T-1 TOF	TYR-T-1 HMW	HAD-B-1 TOF	HAD-B-1 HMW	CER-T-2 TOF	CER-T-2 HMW
Asp	21.6	12.7	8.8	9.8	12.6	11.9
Thr	3.7	5.3	1.8	4.5	5.3	11.1
Ser	21.4	12.9	29.8	12.4	11.4	12.1
Glu	5.1	1.8	7.0	15.6	18.4	14.6
Gly	7.5	25.6	3.6	16.0	14.7	18.4
Ala	4.5	18.1	36.2	13.0	10.5	9.9
Val	34.6	12.8	0.7	2.7	13.5	13.8
Met	0.2	1.0	0.8	0.3	4.6	ndt
Ile	0.8	3.3	1.5	6.5	8.2	3.9
Leu	0.6	6.7	1.5	8.3	0.1	4.3
Tyr	<0.1	<0.1	0.6	2.1	0.2	0.1
Phe	<0.1	<0.1	0.1	8.8	<0.1	0.1

Table 22. Amino acid composition, $\mu M \cdot g^{-1}$ sediment and mole percent (%) for the total organic fraction (TOF) of five sediments from the Judith River Formation, Dinosaur Provincial Park. Owing to the low concentrations of amino acids, actual concentrations are reported to two decimal places. Abbreviations are defined in Tables 16 and 17

AMINO ACID COMPOSITION ($\mu M \cdot g^{-1}$ sediment)

	SED-TOF-1	SED-TOF-2	SED-TOF-3	SED-TOF-4	SED-TOF-5
Asp	0.11	0.06	0.01	0.04	0.01
Thr	0.06	0.01	nd	nd	nd
Ser	0.03	0.03	0.09	0.09	0.03
Glu	0.28	0.13	0.01	0.04	0.03
Gly	0.23	0.18	0.07	0.09	0.04
Ala	0.24	0.13	0.03	0.07	0.04
Val	0.16	0.04	0.01	0.03	0.01
Met	0.04	ndt*	ndt	<0.1	<0.01
Ile	0.02	0.04	0.01	0.02	0.01
Leu	0.01	0.03	0.01	0.03	0.01
Tyr	0.05	ndt	0.01	0.01	<0.01
Phe	ndt	ndt	0.01	0.02	0.02
His	0.01	nd	0.01	0.04	0.01
Lys	0.01	0.04	0.02	nd	0.01
Arg	0.04	nd	nd	nd	nd
TOTAL	1.30	0.70	0.30	0.43	0.23
% AWT	0.02	0.01	nd	nd	nd

AMINO ACID COMPOSITION (mole percent, %)

	SED-TOF-1	SED-TOF-2	SED-TOF-3	SED-TOF-4	SED-TOF-5
Asp	8.9	9.3	3.4	9.6	7.3
Thr	4.9	1.5	nd	nd	nd
Ser	2.4	4.6	35.3	19.6	13.4
Glu	22.8	20.1	3.4	9.8	13.5
Gly	18.7	27.7	27.2	21.6	18.5
Ala	19.5	20.0	12.1	15.0	18.5
Val	13.0	6.2	4.4	6.4	5.4
Met	3.3	ndt	ndt	0.4	1.4
Ile	1.6	6.2	3.1	3.8	7.1
Leu	0.8	4.6	4.3	6.6	5.3
Tyr	4.1	<0.1	2.9	1.9	1.5
Phe	nd	<0.1	4.1	5.0	8.4

Table 23. Amino acid composition, $\mu M \cdot g\ HMW^{-1}$ material and mole percent (%), and yield of high molecular weight (HMW) material isolated from five sediments from the Judith River Formation, Dinosaur Provincial Park. Abbreviations are defined in Tables 16 and 17.

AMINO ACID CONCENTRATIONS ($\mu M \cdot g\ HMW^{-1}$)

	SED-HMW-1	SED-HMW-2	SED-HMW-3	SED-HMW-4	SED-HMW-6
Asp	<0.1	<0.1	<0.1	<0.1	0.8
Thr	0.1	0.1	ndt	<0.1	0.7
Ser	0.1	0.1	0.1	0.1	1.0
Glu	0.1	0.1	<0.1	<0.1	1.3
Gly	0.2	0.2	0.1	0.1	1.7
Ala	0.2	0.2	<0.1	0.1	1.5
Val	0.1	0.1	<0.1	<0.1	1.4
Met	ndt	<0.1	ndt	ndt	ndt
Ile	<0.1	<0.1	<0.1	<0.1	0.3
Leu	0.1	0.1	<0.1	<0.1	0.4
Tyr	<0.1	<0.1	<0.1	<0.1	0.4
Phe	<0.1	<0.1	<0.1	<0.1	0.3
His	nd	nd	nd	nd	nd
Lys	<0.1	nd	nd	nd	0.4
Arg	nd	nd	nd	nd	0.3
TOTAL	0.70	1.00	0.26	0.44	10.44
% AWT	0.01	0.01	<0.01	<0.01	0.12
% HMW	48.8	25.5	37.1	40.20	nd

AMINO ACID CONCENTRATIONS (mole percent, %)

	SED-HMW-1	SED-HMW-2	SED-HMW-3	SED-HMW-4	SED-HMW-6
Asp	2.0	2.9	3.1	1.7	8.1
Thr	6.7	5.7	nd	6.2	7.4
Ser	12.2	14.5	28.0	17.6	10.1
Glu	8.7	9.4	5.4	5.7	13.8
Gly	24.1	22.5	25.4	25.1	17.6
Ala	23.3	22.1	13.9	19.2	15.2
Val	6.7	6.2	3.5	5.5	14.5
Met	nd	0.5	nd	nd	nd
Ile	3.5	3.6	3.9	3.9	3.0
Leu	8.2	7.2	5.5	7.3	3.7
Tyr	0.5	2.3	2.4	4.8	3.8
Phe	2.7	2.8	8.9	3.0	2.7

Table 24. Amino acid composition (mole percent, %) of the low molecular weight (LMW) fraction from sediments.

	AMINO ACID COMPOSITION (mole percent, %)			
	SED-LMW-1	SED-LMW-2	SED-LMW-3	SED-LMW-4
Asp	11.3	12.5	3.5	13.8
Thr	3.9	0.2	ndt[f]	ndt
Ser	<0.1	0.2	39.4	20.1
Glu	27.2	25.2	2.3	11.8
Gly	15.6	29.1	28.1	19.0
Ala	17.0	17.5	11.1	12.2
Val	14.3	5.7	4.9	6.5
Met	4.4	ndt	ndt	0.6
Ile	0.8	7.3	2.7	3.6
Leu	<0.1	2.7	3.6	6.1
Tyr	5.4	ndt	3.0	0.3
Phe	ndt	ndt	1.5	6.1

[f] ndt = not detected

Table 25. Amino acid composition ($\mu M \cdot g^{-1}$ and mole percent, %) for a nonporous and porous sample of the ceratopsid bone CER-B-3. Abbreviations are defined in Tables 16 and 17.

AMINO ACID CONCENTRATIONS ($\mu M \cdot g$ HMW^{-1})
CER-B-3

	POROUS	NONPOROUS
Asp	0.3	0.0
Thr	nd	nd
Ser	0.5	0.1
Glu	0.4	0.0
Gly	1.0	0.3
Ala	0.4	0.1
Val	0.1	0.0
Met	nd	nd
Ile	0.1	0.0
Leu	0.1	0.0
Tyr	0.1	nd
Phe	0.1	0.0
His	nd	nd
Lys	0.1	0.0
Arg	nd	nd
TOTAL	3.1	0.7

MOLE PERCENT (%)¥
CER-B-3

	POROUS	NONPOROUS	POROUS-NONPOROUS
Asp	10.6	6.2	-4.4
Thr	nd	nd	nd
Ser	15.1	17.0	1.9
Glu	12.0	4.1	-8.0
Gly	31.8	36.5	4.7
Ala	13.2	14.5	1.3
Val	3.4	6.1	2.7
Ile	2.7	5.7	2.9
Leu	4.5	5.9	1.4
Tyr	3.6	nd	-3.6
Phe	3.1	4.2	1.2

¥ mole percent based on the acidic and neutral amino acids

Table 26. Carbon and nitrogen isotope values for high molecular weight material isolated from Late Cretaceous vertebrate samples. Replicate analyses indicated in parentheses.

Specimen	Sample Code	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Aquatic Fish			
Amia	AMI-B-1	-26.4	11.6
Teleost	TEL-B-1	-27.0	7.3
Lepisosteid	LEP-B-1	-25.3	7.3
Myledaphus	MYL-T-1	-26.4	6.4
Paralbula	PAR-T-1	-25.2	9.5
Paratarpon	PAT-B-1	-24.3	4.8
Pavement tooth shark	PTS-T-1	-25.3	8.3
Acipenser	STU-T-1	-24.3	5.1
Aquatic Reptiles			
Aspideretes (Trionychid turtle)	ASP-B-2	-23.6(-23.4)	4.6 (4.3)
Champsosaur	CHA-B-1	-23.3	6.2
Champsosaur	CHA-T-1	-24.3	6.4
Plesiosaur	PLE-B-1	-25.3(-25.7)	11.1 (10.9)
Scapherpeton	SCA-B-1	-25.3	7.0
Crocodile	CRO-T-1	-24.7	8.5
Crocodile	CRO-T-2	-23.8	6.3
Crocodile	CRO-T-3	-25.2	6.7
Crocodile	MEAN ± SD	-24.6 ± 0.6	7.2 ± 1.0
Terrestrial Mammal			
Didelphid (opposum)	DIL-B-1	-24.0	0.7
Terrestrial Mesofauna			
Dromaeosaur	DRO-B-1	-23.3	7.9
Ornithomimid	ORN-B-1	-23.2	8.7
Ornithomimid	ORN-B-2	-23.2	5.2
Paleosaniwa	PAL-B-1	-23.8	4.1
Stegoceras	STE-B-1	-24.9	4.6

Table 26. (cont)

Specimen	Sample Code	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Terrestrial Megafauna			
Ceratopsid	CER-B-1	-24.5	7.5
Ceratopsid	CER-B-2	-23.5	8.0
Ceratopsid	CER-B-3	-23.2	-1.0
Ceratopsid	CER-T-1	-24.3	6.4
Ceratopsid	CER-T-2	-24.3(-24.0)	5.3
Ceratopsid	CER-T-3	-24.7	5.2
Ceratopsid	CER-T-4	-23.5	8.5
Ceratopsid	CER-T-5	-23.6	2.9
Ceratopsid	MEAN ± SD*	-24.0 ± 0.5	5.4 ± 3.0
Hadrosaur	HAD-B-1	-24.0	5.2
Hadrosaur	HAD-T-2	-23.8(-23.8)	4.7
Hadrosaur	HAD-T-3	-23.6	4.9
Hadrosaur	HAD-T-4	-24.6	5.0
Hadrosaur	HAD-T-5	-26.0	3.9
Hadrosaur	MEAN ± SD	-24.4 ± 1.0	4.7 ± 0.5
Nodosaur	NOD-T-1	-23.8	6.9
Nodosaur	NOD-T-2	-23.9	
Panoplosaur	PAN-T-1	-27.2	2.3
Tyrannosaur	TYR-B-1	-24.0(-23.8)	6.4(6.1)
Tyrannosaur	TYR-T-1	-24.6	7.2
Tyrannosaur	TYR-T-2	-23.6	6.4
Tyrannosaur	MEAN ± SD	-24.0 ± 0.4	6.6 ± 0.4
Immature tyrannosaur	TYR-T-3	-23.0	11.4
Marine Fauna (Bear Paw Formation)			
Mosasaur	MOS-T-2	-24.6	3.1
Marine Fauna (Niobrara Formation)			
Mosasaur	MOS-B-1	-24.0	5.9
Mosasaur	MOS-T-1	-24.8	4.?
Shark	SHA-T-1	-24.4	4.8

Table 27. Carbon and nitrogen isotopic composition of high molecular weight material isolated from a size series of hadrosaur femora. These samples were obtained as a powder and, therefore, there is no assurance of adequate mechanical cleaning.

Specimen	Sample Code	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Hadrosaur Femora			
765 mm	HAD-F-1	-24.6	-2.4
807 mm	HAD-F-2	-24.0	5.0
960 mm	HAD-F-4	-23.6	-1.4
970 mm	HAD-F-5	-23.6	3.6
977 mm	HAD-F-6	-24.0	3.9
990 mm	HAD-F-7	-24.9	5.4
1030 mm	HAD-F-8	nd*	3.0
1035 mm	HAD-F-9	-19.7	3.2
1050 mm	HAD-F-10	-24.0	3.3
1066 mm	HAD-F-11	-24.3	4.8
1097 mm	HAD-F-12	-23.8	-1.1
1170 mm	HAD-F-13	-23.7	2.3
	MEAN ± SD	-23.6 ± 1.4	2.5 ± 2.6

* nd = not determined

Table 28. Isotope values of total organic fraction (TOF) and high molecular weight (HMW) material from Late Cretaceous fossils. Isotopic shifts ($\Delta\ \delta^{13}C$ and $\Delta\delta^{15}N$) in the HMW material relative to the TOF of fossils are also given. Replicate analyses indicated in parentheses.

Sample Code	Organic Fraction	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\Delta^{13}C^{*}$	$\Delta^{15}N^{\nabla}$
Sturgeon					
STU-T-1	TOF	-20.3	12.0	-4.0	-6.9
STU-T-1	HMW	-24.3	5.1		
Ceratopsid					
CER-B-2	TOF	-24.2(-24.4)	1.2(1.2)	+0.4	+6.8
CER-B-2	HMW	-23.8	8.0		
CER-T-4	TOF	-24.2 (-24.3)	2.5	-0.1	+2.8
CER-T-4	HMW	-24.3 (-24.3)	5.3		
CER-T-5	TOF	-23.1	6.5	+1.6	-1.3
CER-T-5	HMW	-24.7	5.2		
CER-T-7	TOF	-24.3	15.5	+1.3	-12.4
CER-T-7	HMW	-23.6	2.9		
Hadrosaur					
HAD-B-1	TOF	-27.3	8.2	+3.3	-3.1
HAD-B-1	HMW	-24.0	5.1		
HAD-T-2	TOF	-23.3	nd	+0.5	
HAD-T-2	HMW	-23.8	4.7		
HAD-T-3	TOF	-23.1	14.9	-1.5	-9.9
HAD-T-3	HMW	-24.6	5.0		
Tyrannosaur					
TYR-B-1	TOF	-25.5	4.7	-0.3	+1.6
TYR-B-1	HMW	-24.7	6.4(6.1)		
TYR-T-1	TOF	-23.9	14.1	-0.5	-6.9
TYR-T-1	HMW	-24.6	7.2		
Ornithomimid					
ORN-B-1	TOF	-21.7			-1.5
ORN-B-1	HMW	-23.2	8.7		
			MEAN	-0.1	-2.9
			SD	±1.9	±5.8

Table 29. Isotope values of total organic fraction (TOF) of Late Cretaceous flora TOF and high molecular weight material (HMW) from sediments. Isotopic shifts ($\Delta\ \delta^{13}C$ and $\Delta\delta^{15}N$) in the HMW material relative to the TOF of sediments are also given.

Sample Code	Organic Fraction	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\Delta^{13}C^{*}$	$\Delta^{15}N^{¥}$
Flora					
TAX-V-1 (Taxid)		-26.3	4.1		
THU-V-1 (Thuja)		-25.6	6.1		
Sediments					
SED-TOF-1	TOF	-24.0	6.1	-1.0	-3.1
SED-HMW-1	HMW	-25.0	3.0		
SED-TOF-2	TOF	-24.4	5.7	0.0	-4.0
SED-HMW-2	HMW	-24.4	1.7		
SED-TOF-3	TOF	-25.1	5.6	+0.6	-4.1
SED-HMW-3	HMW	-24.5	1.5		
SED-TOF-4	TOF	-25.2	7.8	+1.3	-6.3
SED-HMW-4	HMW	-23.9	0.5		
SED-TOF-5	TOF	-24.1	6.3	0.0	-4.2
SED-HMW-5	HMW	-24.1	2.1		
MEAN	TOF	-24.6 ± 0.6	6.3 ± 0.9		
MEAN	HMW	-24.4 ± 0.4	2.2 ± 1.4		
			MEAN	+0.2	-4.5
			SD	±0.8	±1.4

* $\Delta^{13}C = \delta^{13}C_{HMW} - \delta^{13}C_{TOF}$
¥ $\Delta^{15}N = \delta^{15}N_{HMW} - \delta^{15}N_{TOF}$
** SD = standard deviation

Table 30. Isotopic compositions of consumers from a freshwater subtropical ecosystem: Everglades National Park, Florida (Ostrom, unpublished data). Analysis was performed on the muscle tissue of the gar and whole bodies of all other fish.

Taxa (common name)	Standard Length (mm)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)
Gambusia affinis	28, 29	-29.1	8.4
(mosquitofish)	17 to 20	-29.6	8.2
	23 to 28	-28.7	9.5
	23 to 28	nd	9.6
	average:	-29.1 ± 0.5	8.9 ± 0.7
Ictalurus notatus			
(Yellow bullhead)	87	-28.5	7.9
Lepisosteus platyrhincus			
(gar)	45	-27.7	10.9
Lepomis punctatus			
(spotted sunfish)	83	nd*	9.9
	94	-26.0	9.3
Lucania goodei			
(bluefin killifish)		-29.2	8.7
Poecilia latipinna	39	nd	8.2
(sailfin molly)	59	-30.4	8.7

* nd = not determined

Figure 1. Map of bone bed localities in Dinosaur Provincial Park. Closed circles with labels refer to locations of bone beds and microsites listed in Tables 1 and 2 (based on Brinkman, in press). See Appendix 4 for stratigraphic correlation.

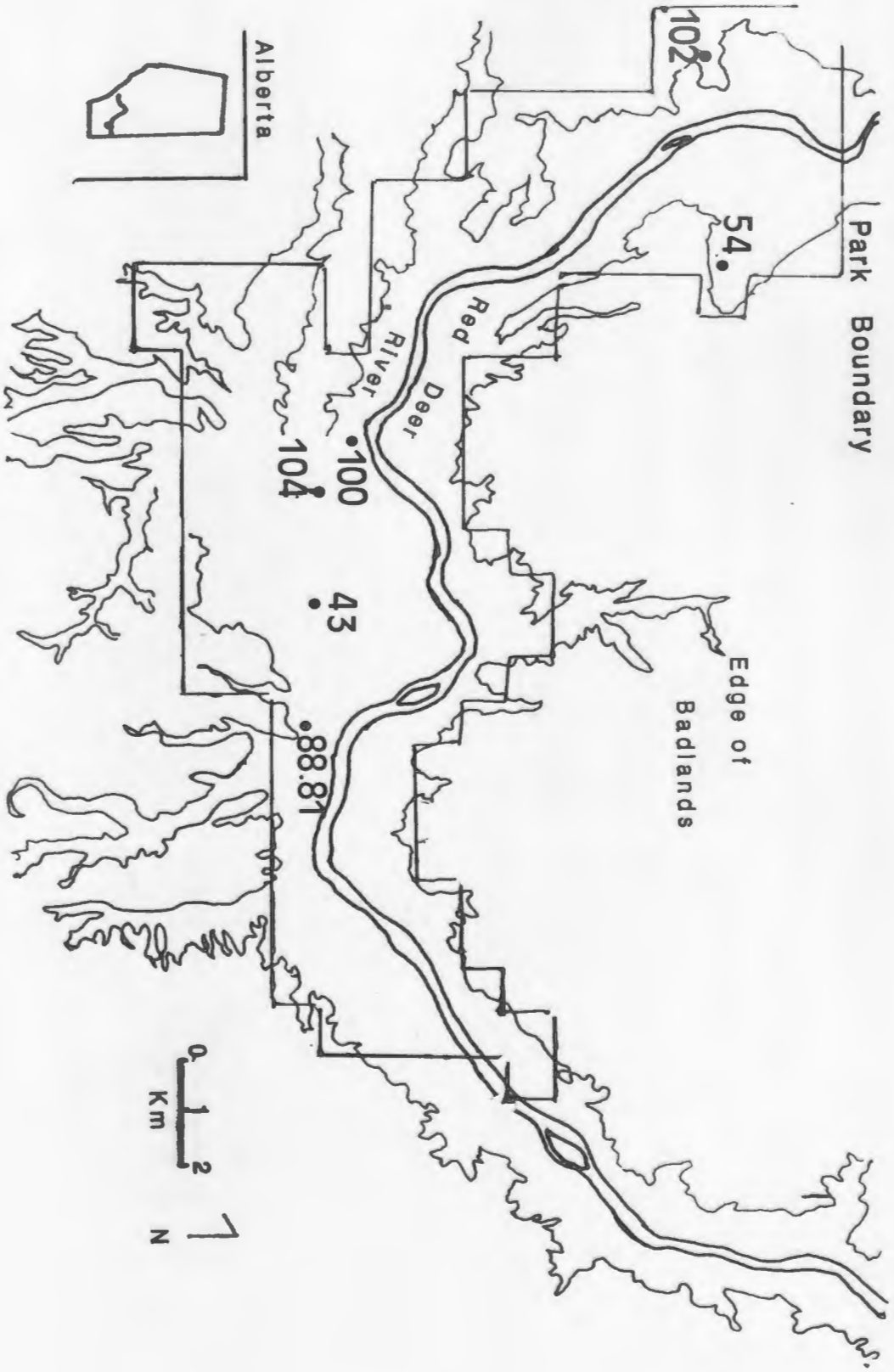

Alberta
Park Boundary
102
54
Red Deer River
100
104
43
88.81
Edge of Badlands
0 1 2
Km
N

Figure 2. Carbon and nitrogen isotopic composition of collagen from prehistoric marine and terrestrial fauna (data taken from DeNiro, 1985; Nelson et al., 1986).

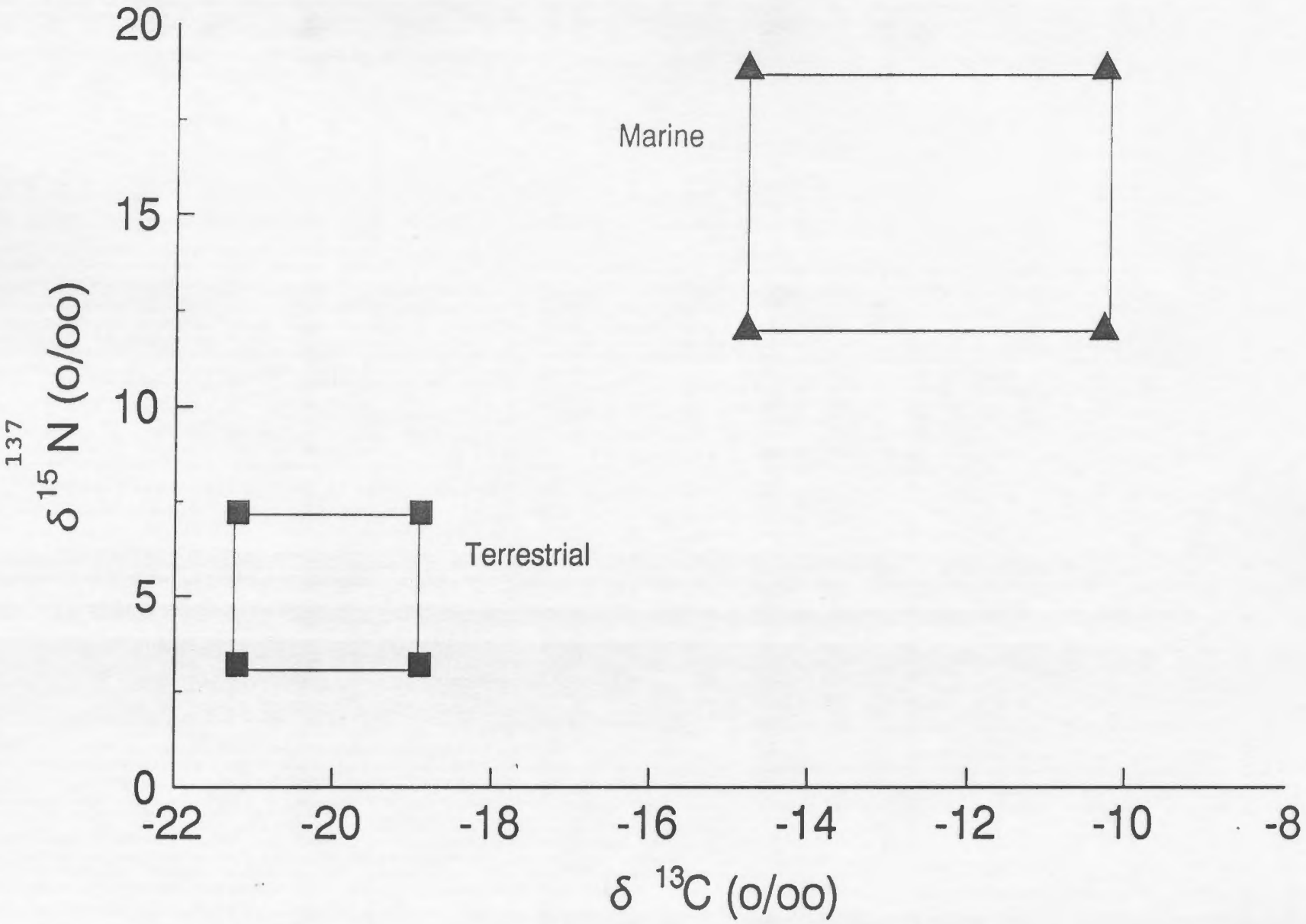
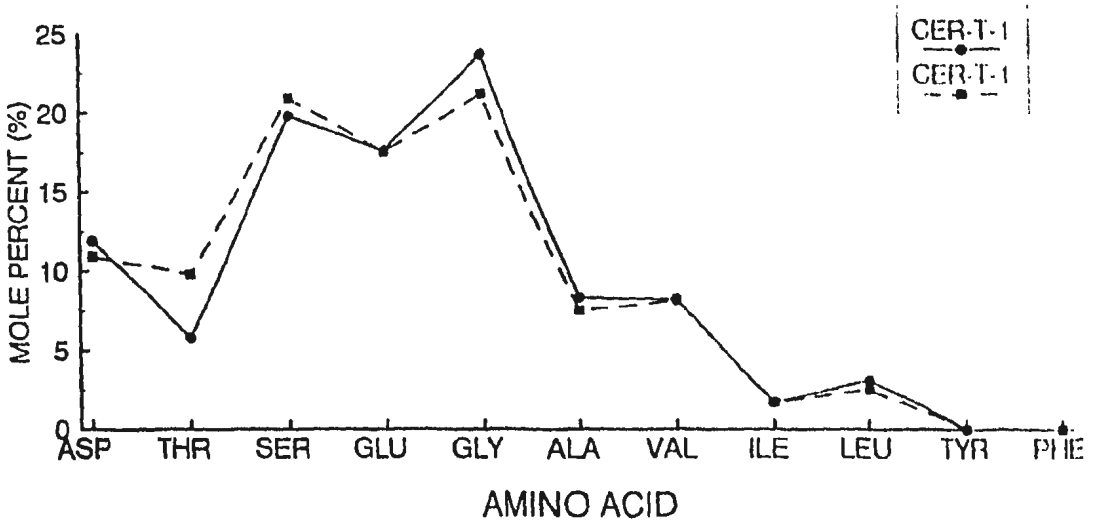
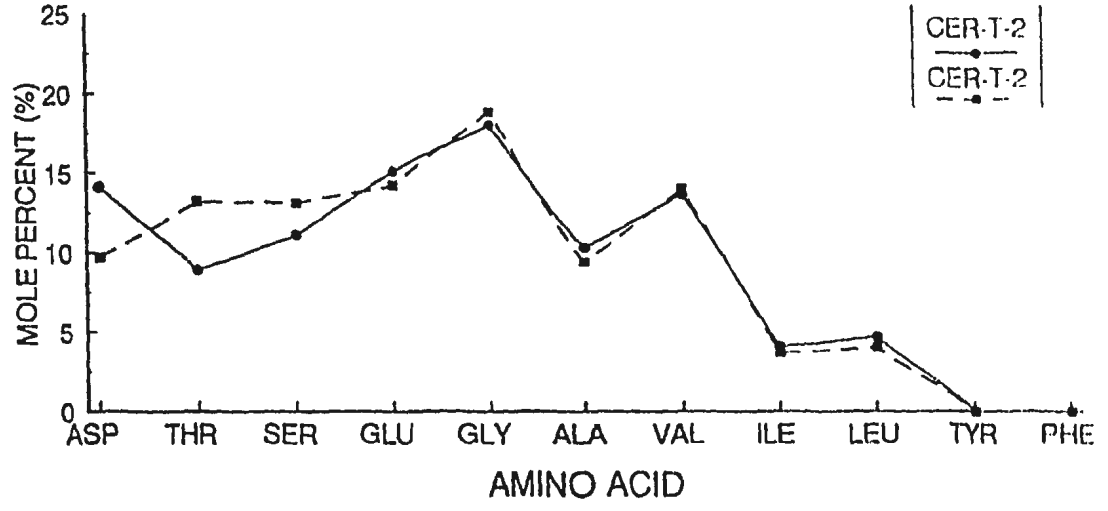

20
15
10
5
0
-22
-20
-18
-16
-14
-12
-10
-8
Marine
Terrestrial
δ 15 N (o/oo)
137
δ 13C (o/oo)

Figure 3. Replicate analyses of amino acid composition (mole percent) for high molecular weight material isolated from ceratopsid teeth, CER-T-1 and CER-T-2 and a hadrosaur tooth, HAD-T-1. A value of zero is indicated for amino acids which were not detected.


CER-T-1
CER-T-1
MOLE PERCENT (%)
25
20
15
10
5
0
ASP
THR
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID


CER-T-2
CER-T-2
MOLE PERCENT (%)
25
20
15
10
5
0
ASP
THR
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID

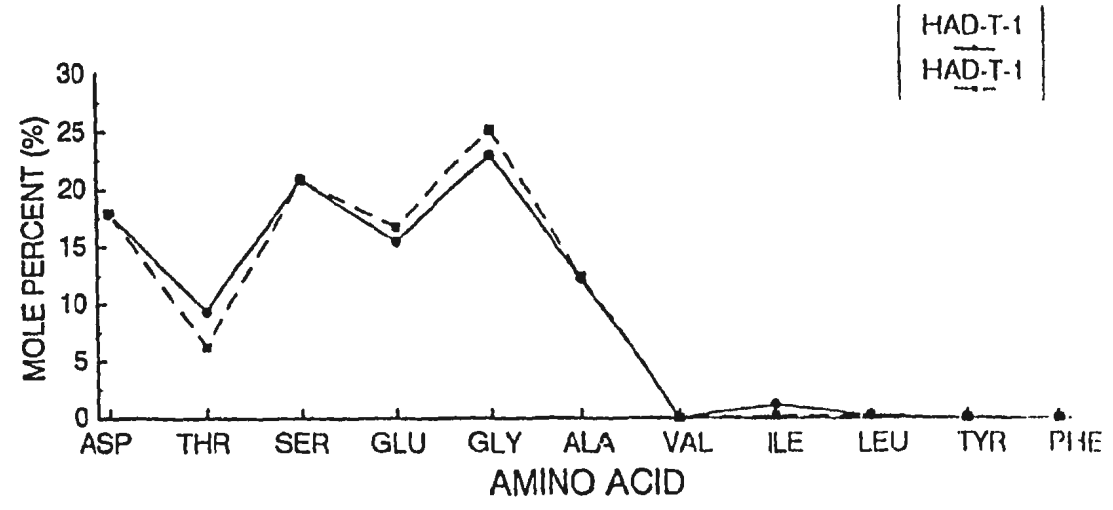

HAD-T-1
HAD-T-1
MOLE PERCENT (%)
30
25
20
15
10
5
0
ASP
THR
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID

Figure 4. Amino acid composition (mole percent) of HMW material from the bones of a modern cow, a ceratopsid (CER-B-1) a hadrosaur (HAD-B-1) and a tyrannosaur (TYR-B-1). A value of zero is indicated for amino acids which were not detected.

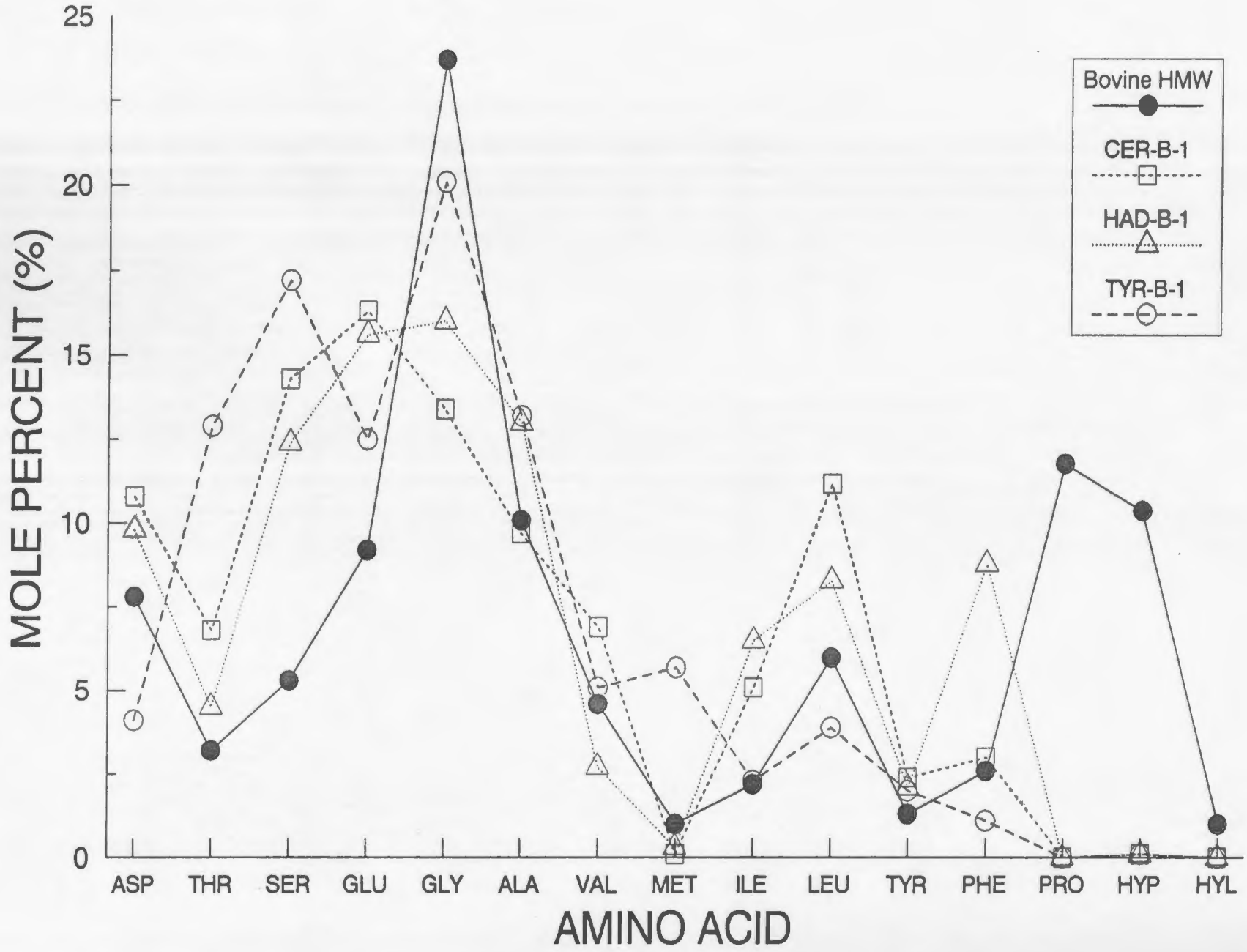

MOLE PERCENT (%)
25
20
15
10
5
0
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
PRO
HYP
HYL
AMINO ACID
Bovine HMW
CER-B-1
HAD-B-1
TYR-B-1

Figure 5. Amino acid composition (mole percent) of high molecular weight material from five ceratopsid teeth. A value of zero is indicated for amino acids which were not detected.

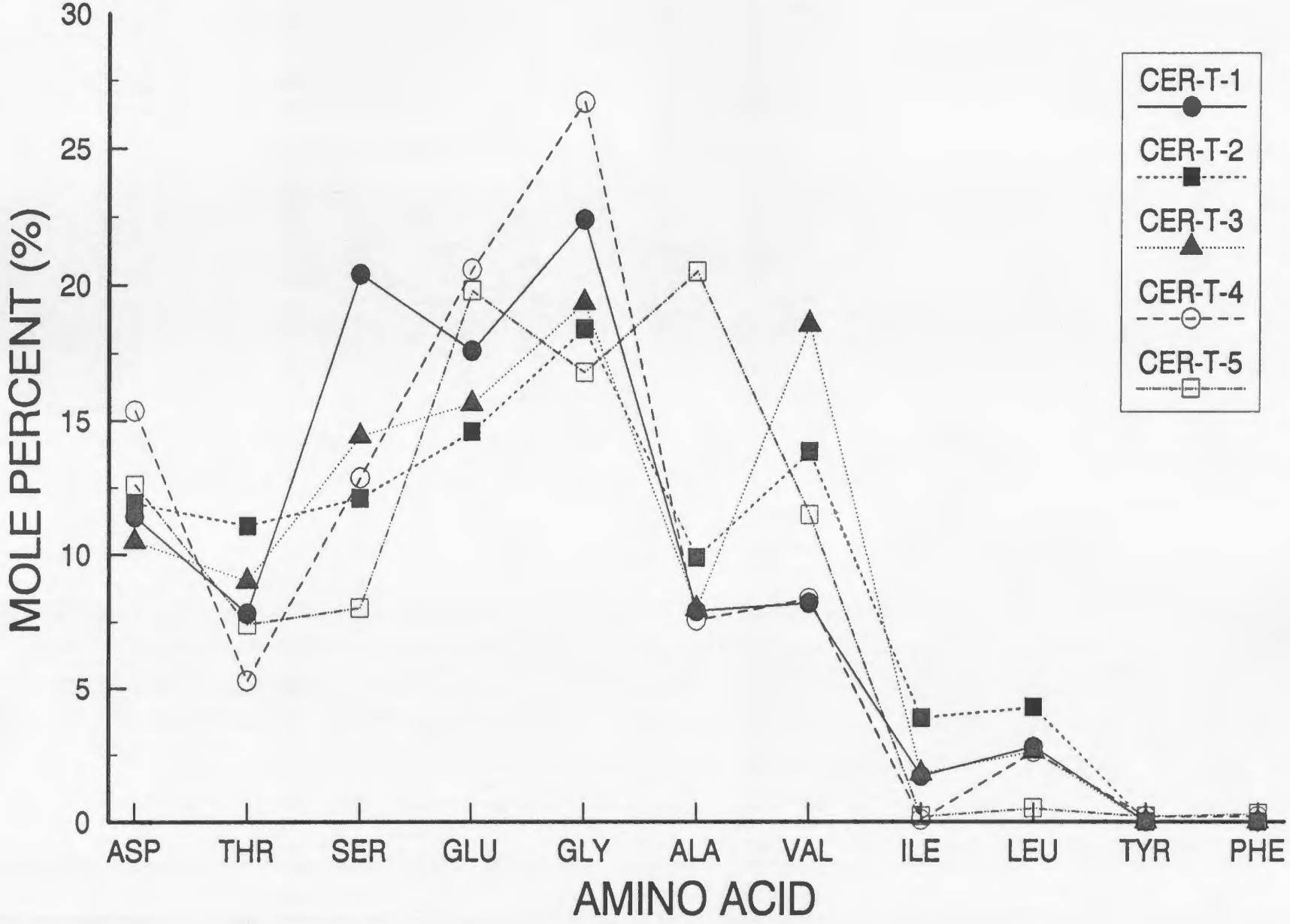

30
25
20
15
10
5
0
MOLE PERCENT (%)
ASP
THR
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID
CER-T-1
CER-T-2
CER-T-3
CER-T-4
CER-T-5

Figure 6. Amino acid composition (mole percent) of high molecular weight material from four hadrosaur teeth. A value of zero is indicated for amino acids which were not detected.

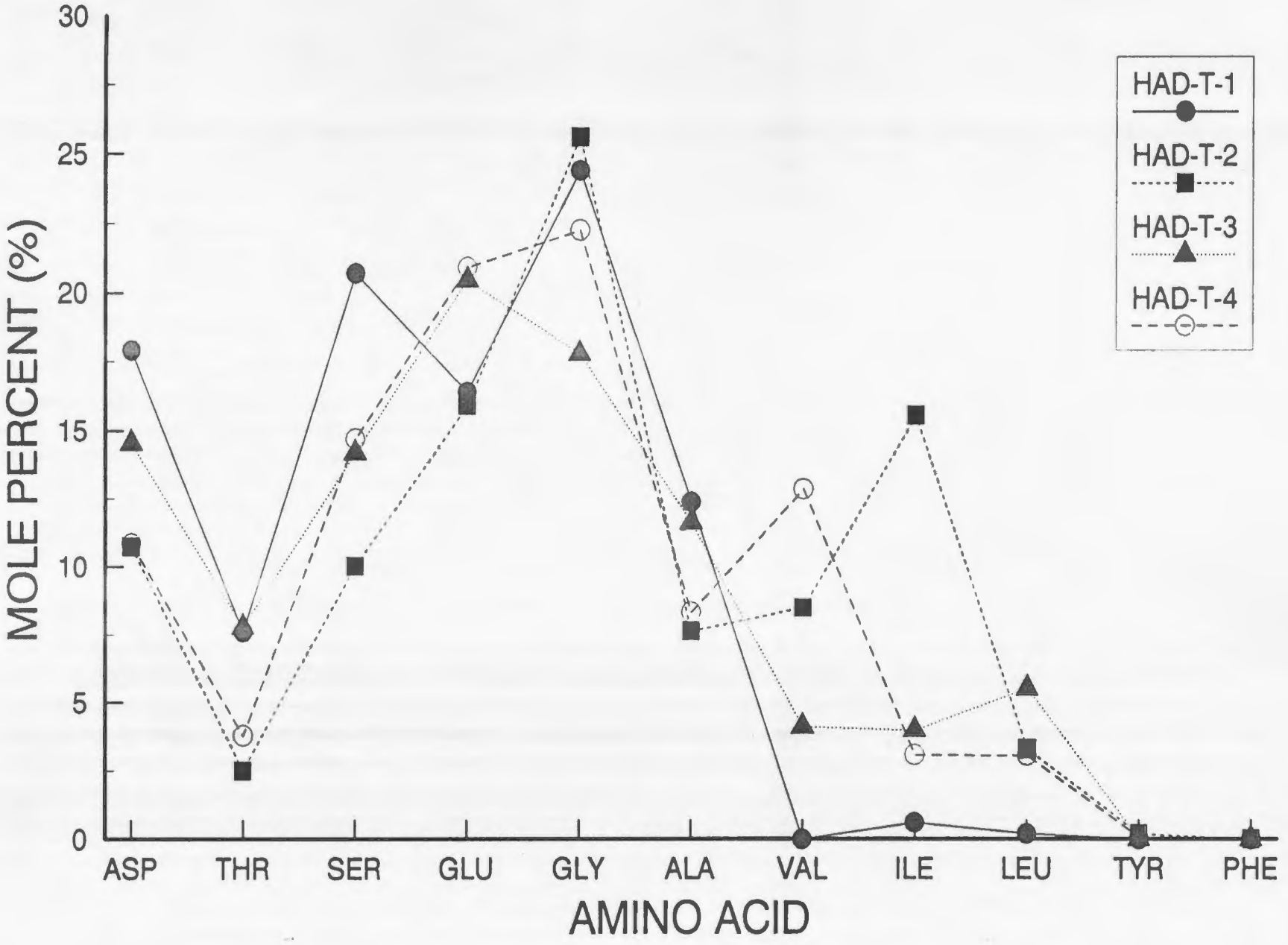

30
25
20
15
10
5
0
MOLE PERCENT (%)
ASP
THR
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID
HAD-T-1
HAD-T-2
HAD-T-3
HAD-T-4

Figure 7. Amino acid composition (mole percent) of high two molecular weight material from two tyrannosaur teeth. A value of zero is indicated for amino acids which were not detected.

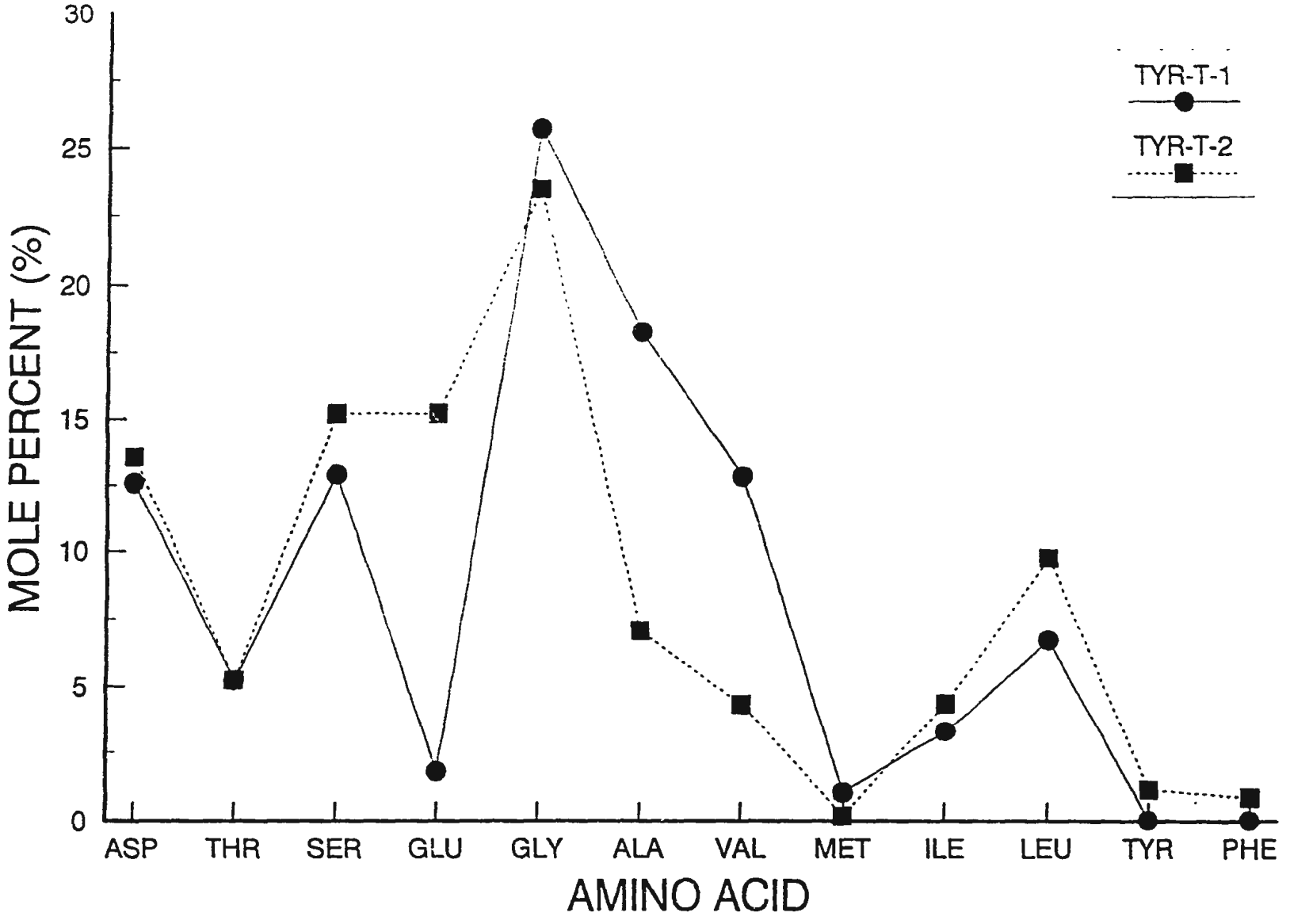
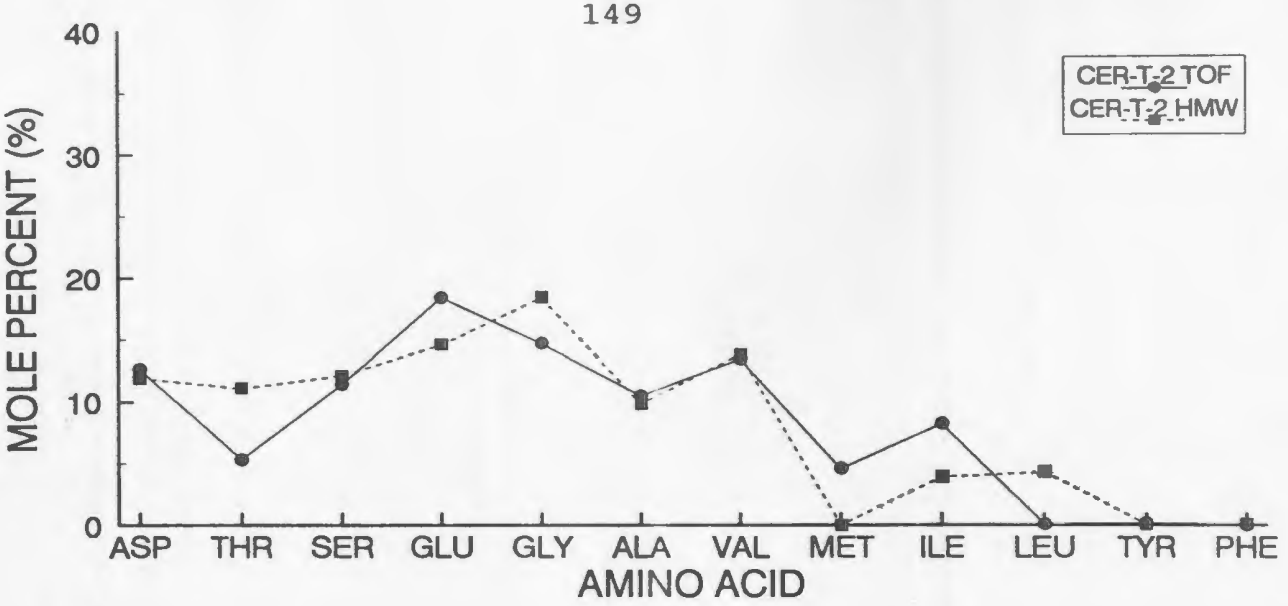
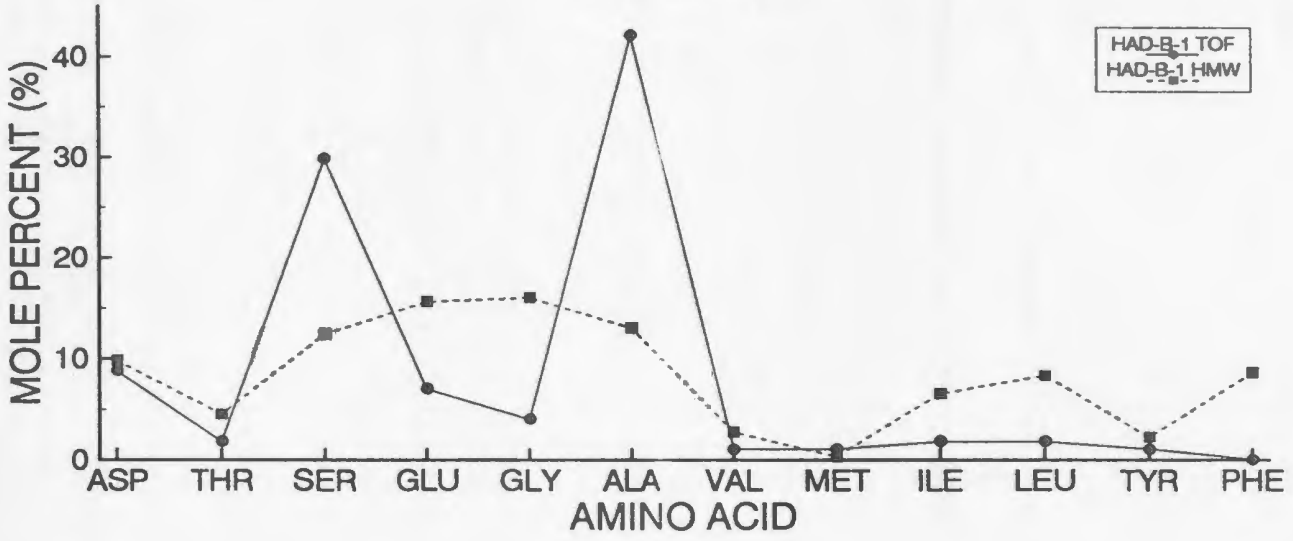

30
25
20
15
10
5
0
MOLE PERCENT (%)
TYR-T-1
TYR-T-2
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

Figure 8. Amino acid composition (mole percent) of the total organic fraction (TOF) and high molecular material (HMW) from a hadrosaur bone, HAD-B-1, a ceratopsid tooth, CER-T-2, and tyrannosaurtooth, TYR-T-1. A value of zero is indicated for amino acids which were not detected.


CER-T-2 TOF
CER-T-2 HMW
MOLE PERCENT (%)
0
10
20
30
40
ASP THR SER GLU GLY ALA VAL MET ILE LEU TYR PHE
AMINO ACID


HAD-B-1 TOF
HAD-B-1 HMW
MOLE PERCENT (%)
0
10
20
30
40
ASP THR SER GLU GLY ALA VAL MET ILE LEU TYR PHE
AMINO ACID

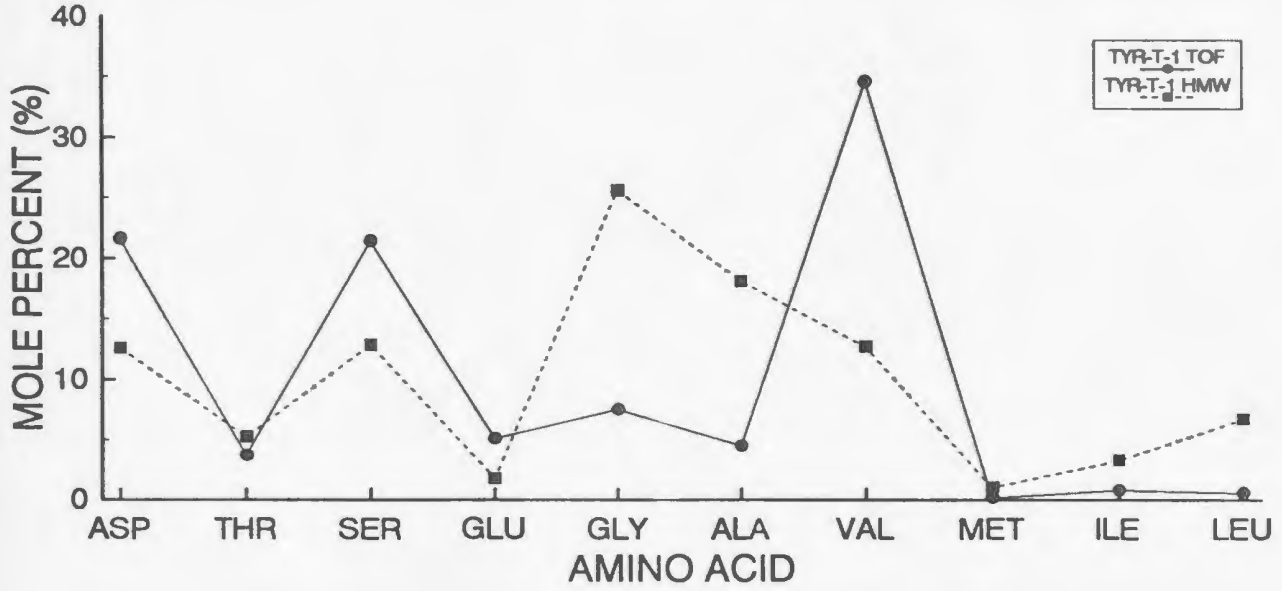

TYR-T-1 TOF
TYR-T-1 HMW
MOLE PERCENT (%)
0
10
20
30
40
ASP THR SER GLU GLY ALA VAL MET ILE LEU
AMINO ACID

Figure 9. Difference in amino acid composition (mole percent) between the high molecular weight (HMW) and total organic fraction (TOF) of a tyrannosaur tooth, TYR-T-1, a hadrosaur bone, HAD-B-1, and a ceratopsid tooth, CER-T-2.

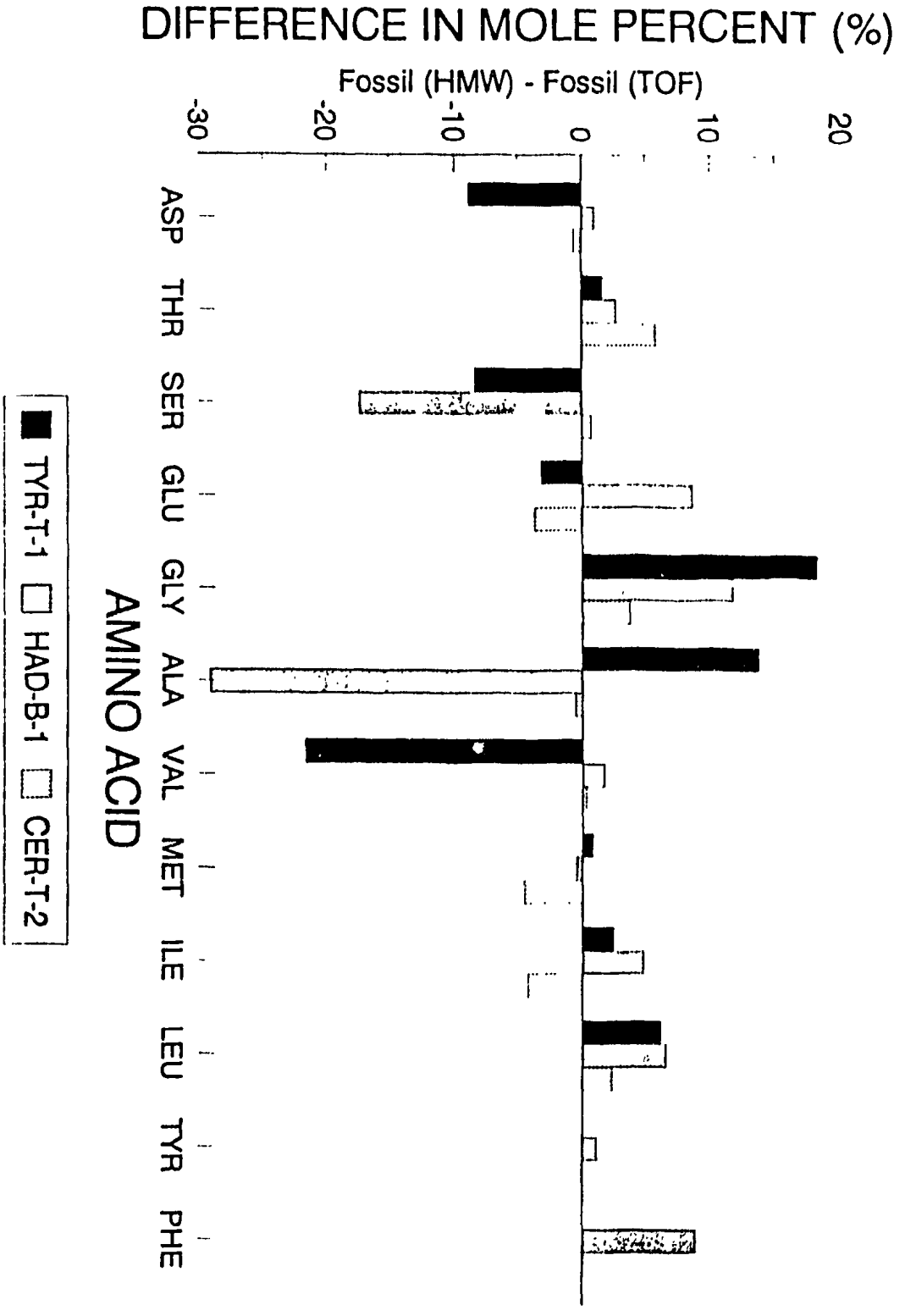
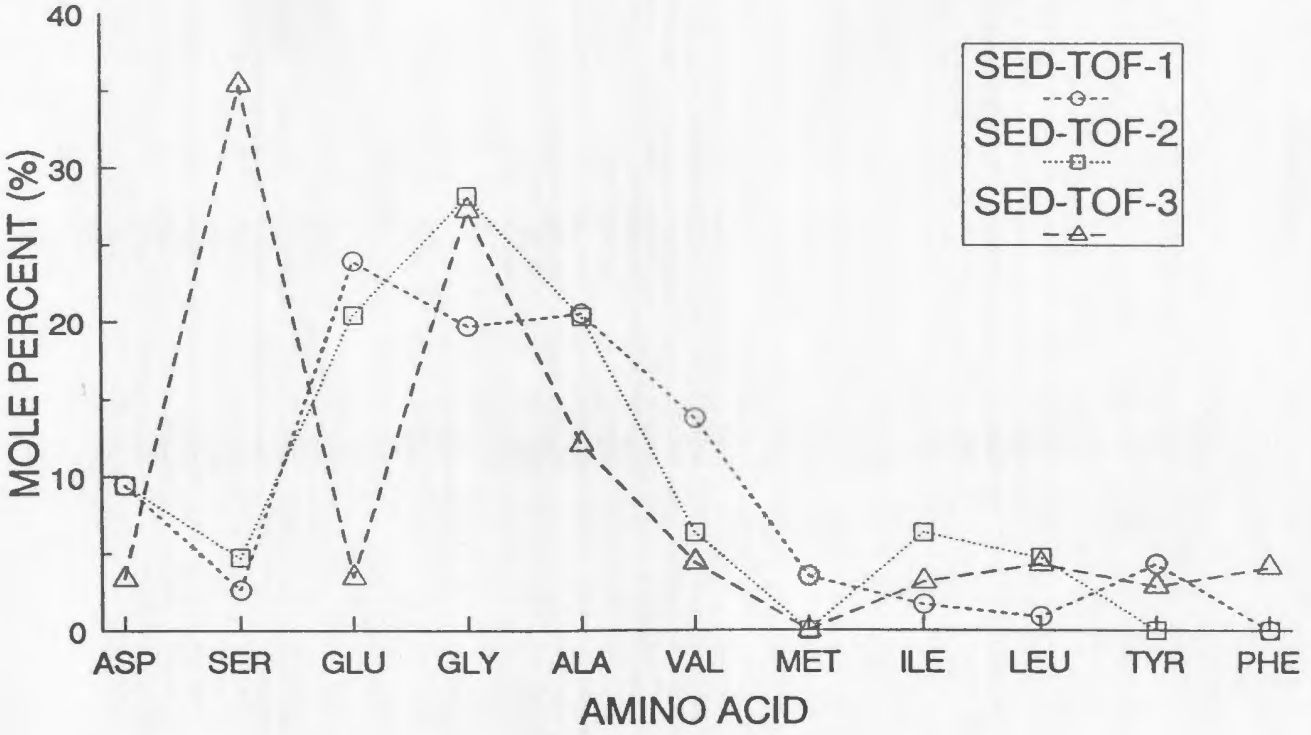

DIFFERENCE IN MOLE PERCENT (%)
Fossil (HMW) - Fossil (TOF)
-30
-20
-10
0
10
20
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID
TYR-T-1
HAD-B-1
CER-T-2

Figure 10. Amino acid composition (mole percent) of the total organic fraction from five sediments. A value of zero is indicated for amino acids which were not detected.


SED-TOF-1
SED-TOF-2
SED-TOF-3
MOLE PERCENT (%)
0
10
20
30
40
ASP
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

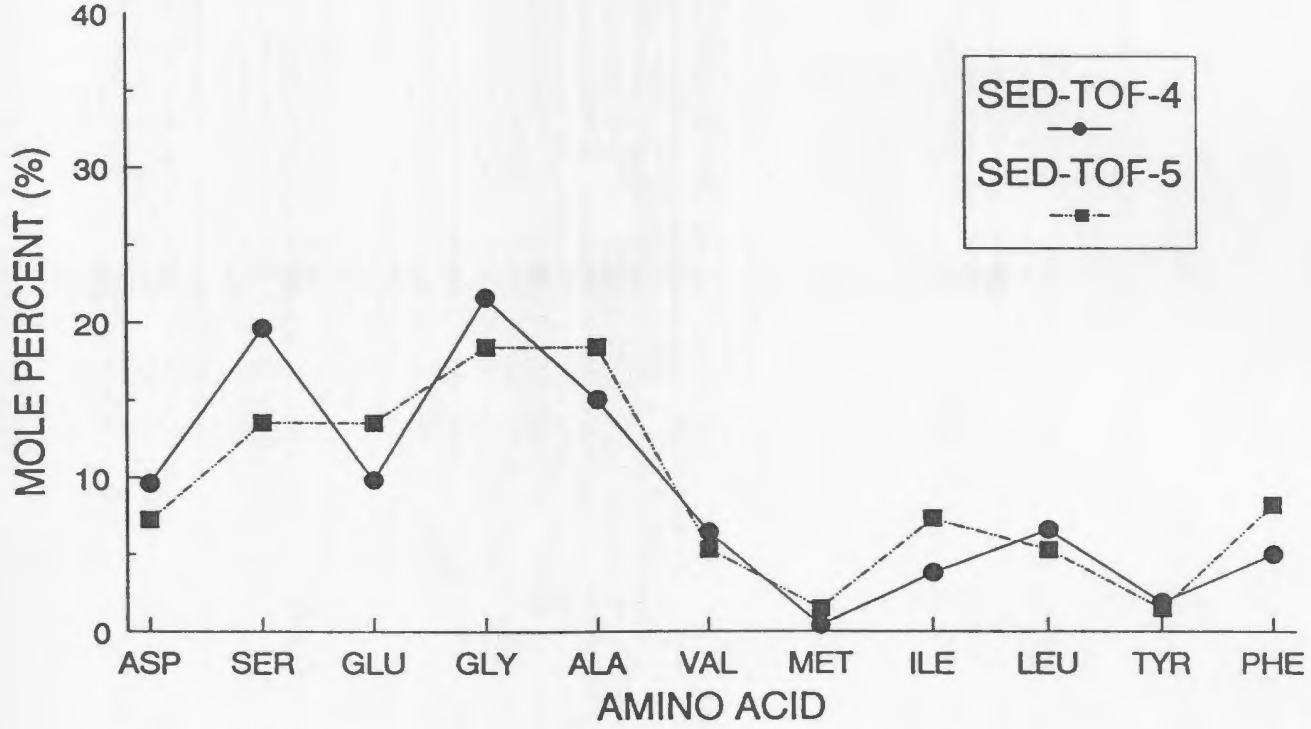

SED-TOF-4
SED-TOF-5
MOLE PERCENT (%)
0
10
20
30
40
ASP
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

Figure 11. Amino acid composition (mole percent) of the high molecular weight material from five sediments. A value of zero is indicated for amino acids which were not detected.

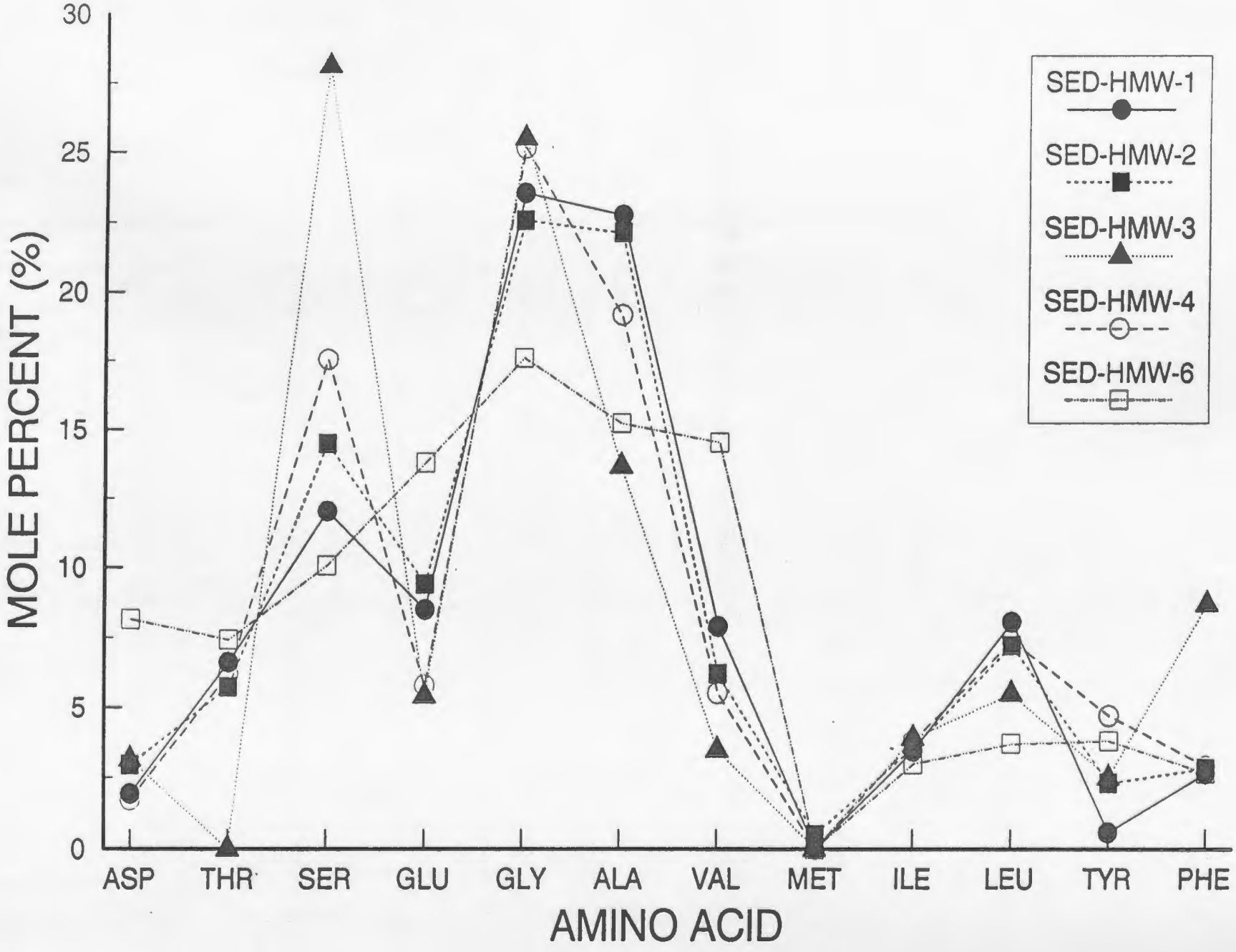

30
25
20
15
10
5
0
MOLE PERCENT (%)
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID
SED-HMW-1
SED-HMW-2
SED-HMW-3
SED-HMW-4
SED-HMW-6

Figure 12. Difference in the relative abundance of amino acids (mole percent) between the high molecular weight fraction (HMW) and total organic fraction (TOF) for four sediments.

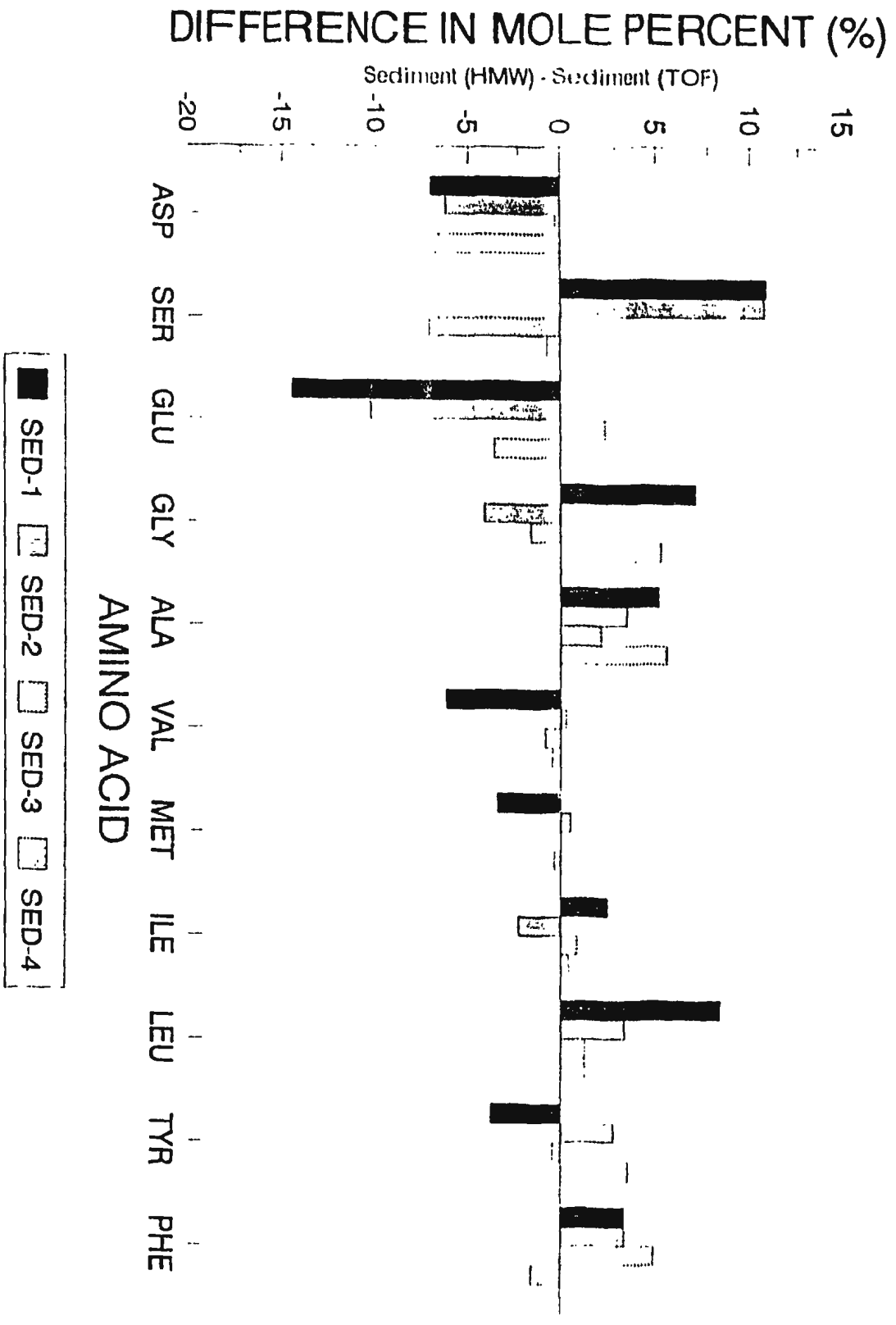
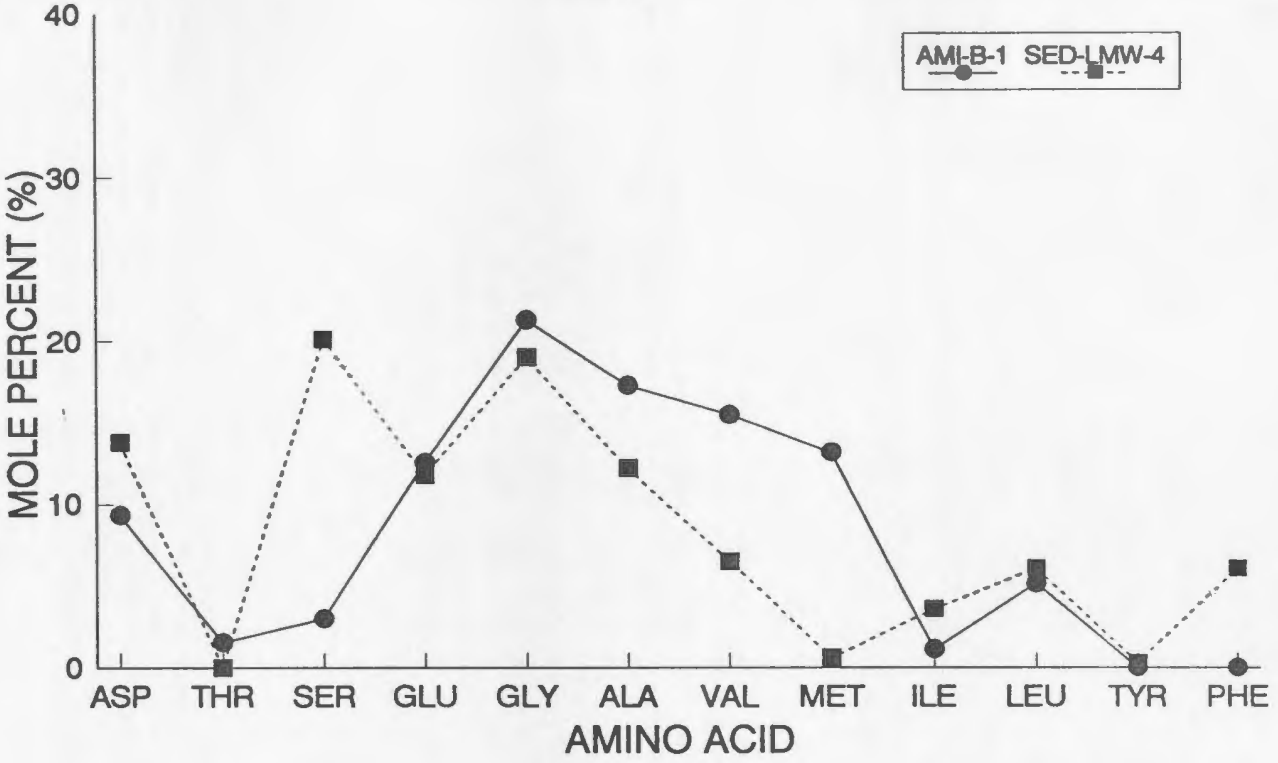

DIFFERENCE IN MOLE PERCENT (%)
Sediment (HMW) - Sediment (TOF)
-20
-15
-10
-5
0
5
10
15
ASP
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID
SED-1
SED-2
SED-3
SED-4

Figure 13. Amino acid composition (mole percent) of high molecular weight (HMW) material from two fossils (AMI-B-1 and CER-B-3) and the low molecular weight (LMW) fraction of the associated sediment. A value of zero is indicated for amino acids which were not detected.


AMI-B-1
SED-LMW-4
MOLE PERCENT (%)
0
10
20
30
40
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

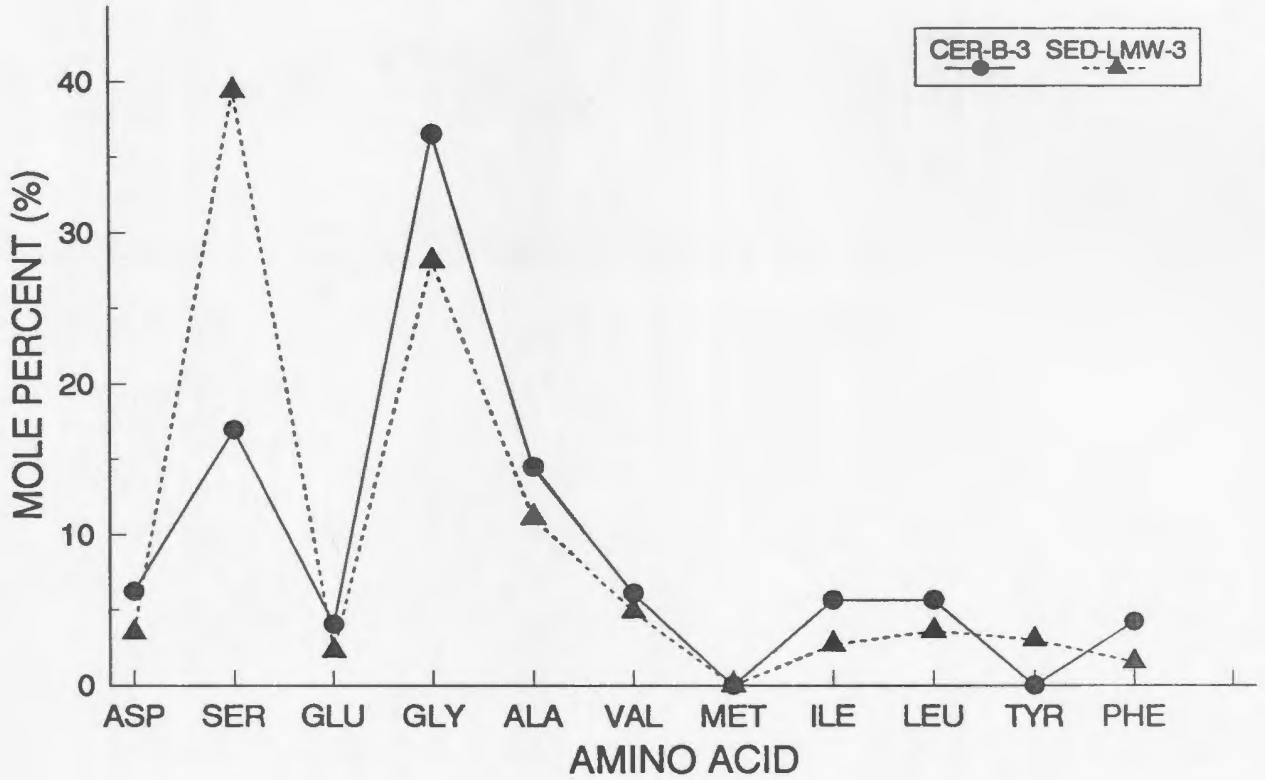
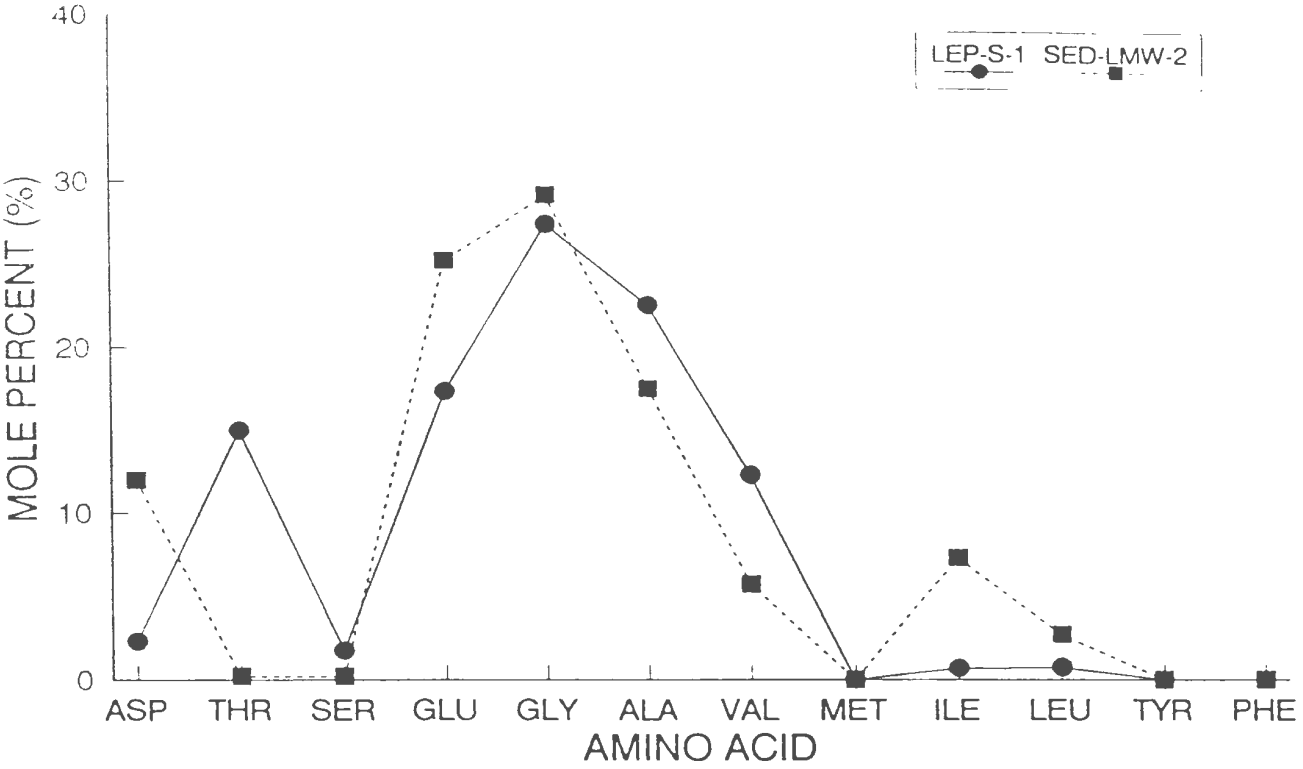

CER-B-3
SED-LMW-3
MOLE PERCENT (%)
0
10
20
30
40
ASP
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

Figure 14. Amino acid composition (mole percent) of high molecular weight (HMW) material from two fossils, LEP-S-1 and TEL-B-1 and the low molecular weight (LMW) fraction of the associated sediment. A value of zero is indicated for amino acids which were not detected.


LEP-S-1 SED-LMW-2
MOLE PERCENT (%)
40
30
20
10
0
ASP THR SER GLU GLY ALA VAL MET ILE LEU TYR PHE
AMINO ACID

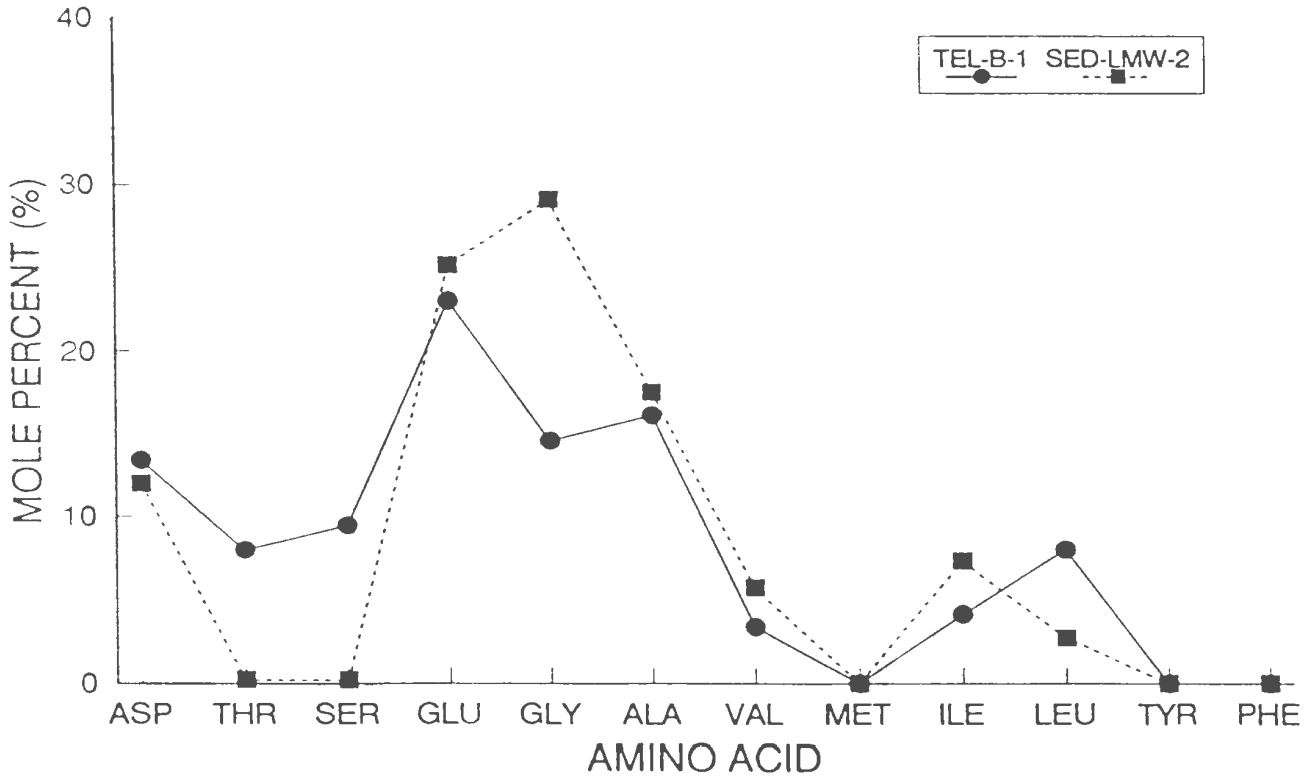

TEL-B-1 SED-LMW-2
MOLE PERCENT (%)
40
30
20
10
0
ASP THR SER GLU GLY ALA VAL MET ILE LEU TYR PHE
AMINO ACID

Figure 15. Difference in the relative abundance of amino acids (mole percent) between the high molecular weight material (HMW) of four fossils and the low molecular weight (LMW) material for associated sediments.

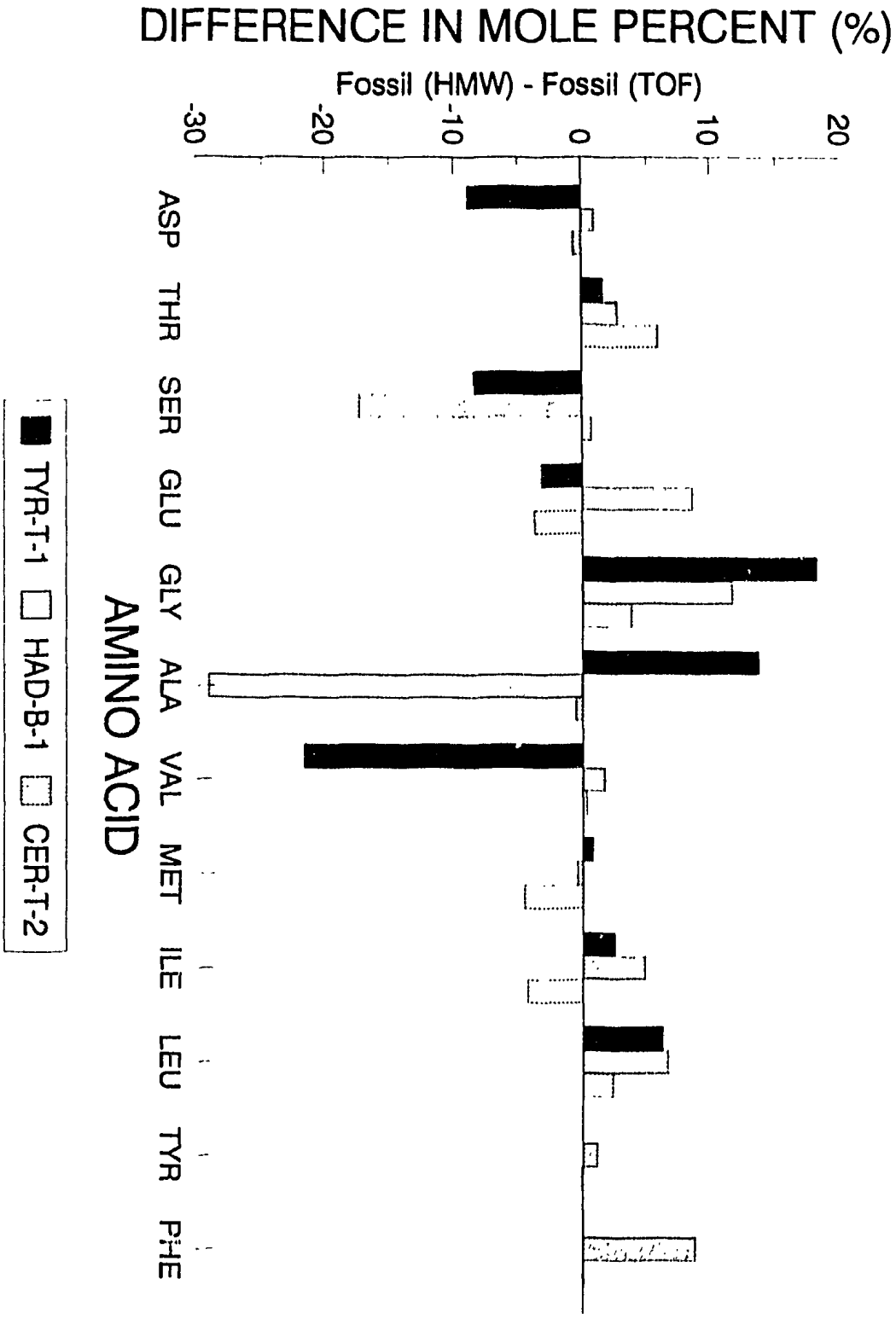
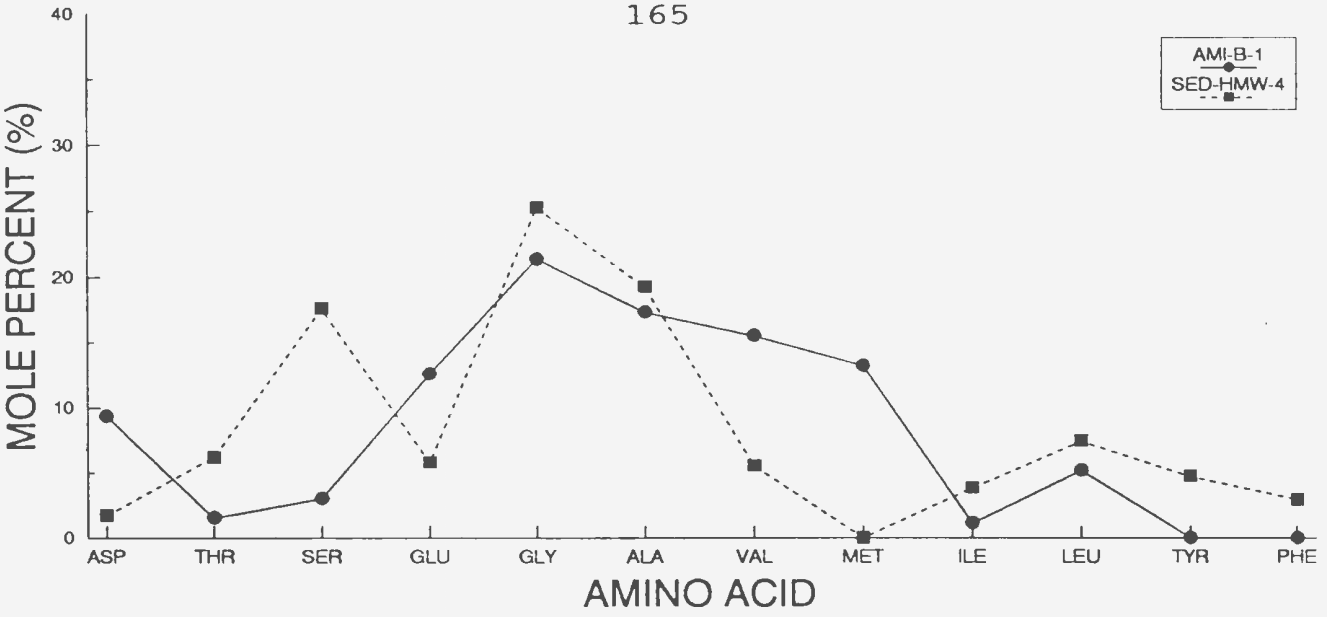
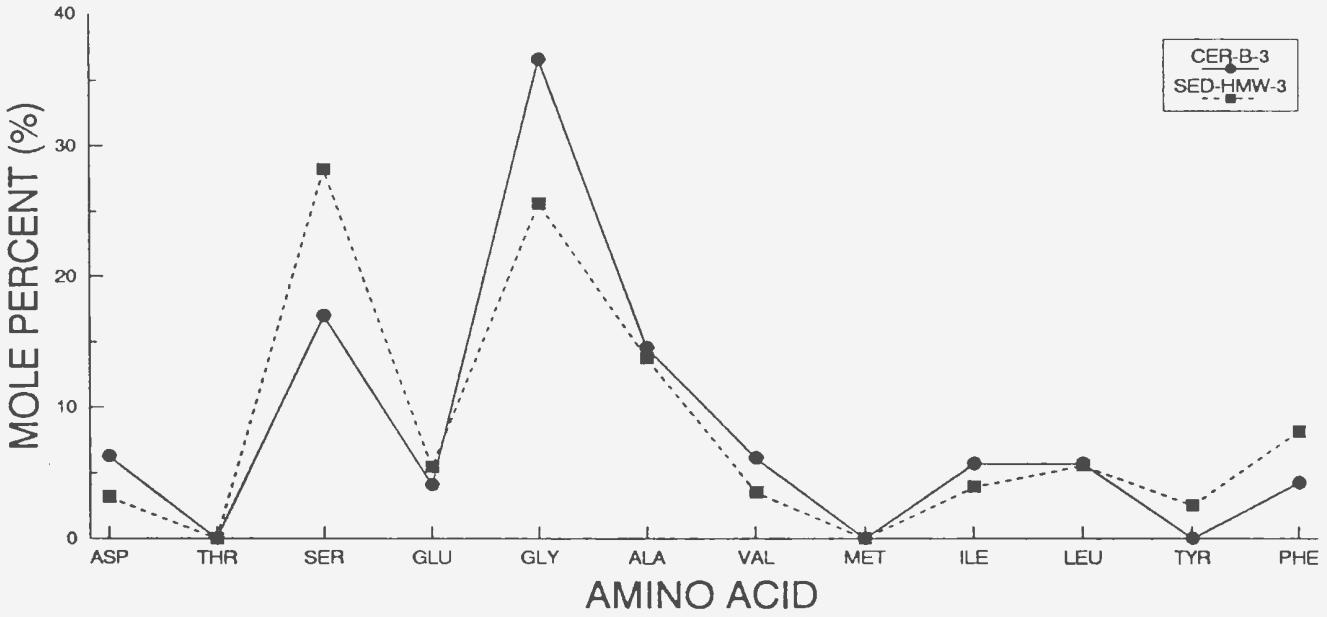

DIFFERENCE IN MOLE PERCENT (%)
Fossil (HMW) - Fossil (TOF)
-30
-20
-10
0
10
20
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID
TYR-T-1
HAD-B-1
CER-T-2

Figure 16. Amino acid composition (mole percent) of high molecular weight material from three fossils (AMI-B-1, CER-B-3, and LEP-S-1) and high molecular weight (HMW) organic material from associated sediment. A value of zero is indicated for amino acids which were not detected.


AMI-B-1
SED-HMW-4
MOLE PERCENT (%)
0
10
20
30
40
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID


CER-B-3
SED-HMW-3
MOLE PERCENT (%)
0
10
20
30
40
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

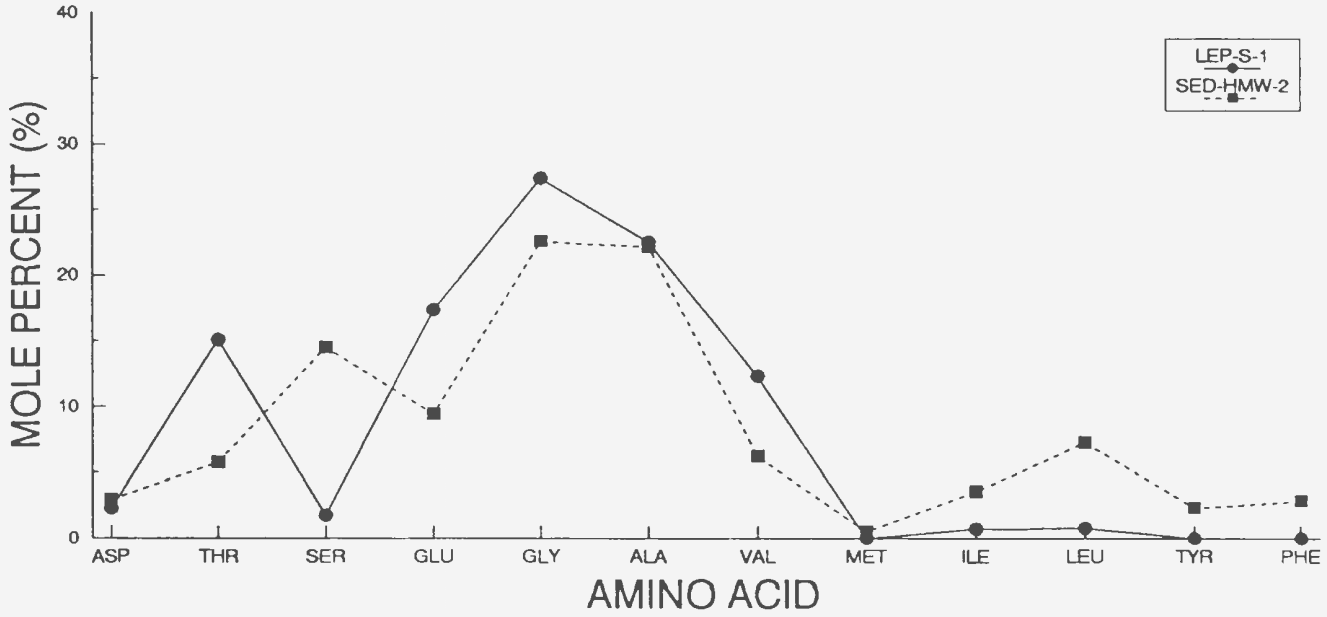
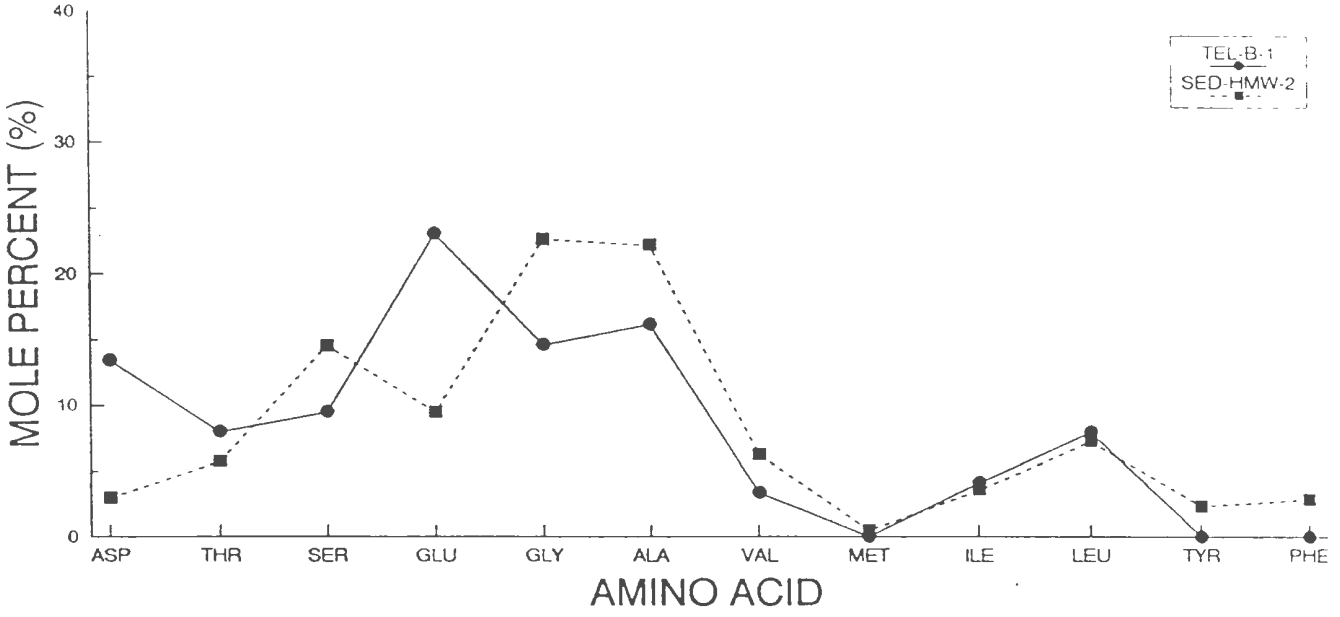

LEP-S-1
SED-HMW-2
MOLE PERCENT (%)
0
10
20
30
40
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

Figure 17. Amino acid composition (mole percent) of high molecular weight material from two fossils, TEL-B-1 and TYR-B-1 and the high molecular weight material of associated sediment. A value of zero is indicated for amino acids which were not detected.


TEL-B-1
SED-HMW-2
MOLE PERCENT (%)
40
30
20
10
0
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

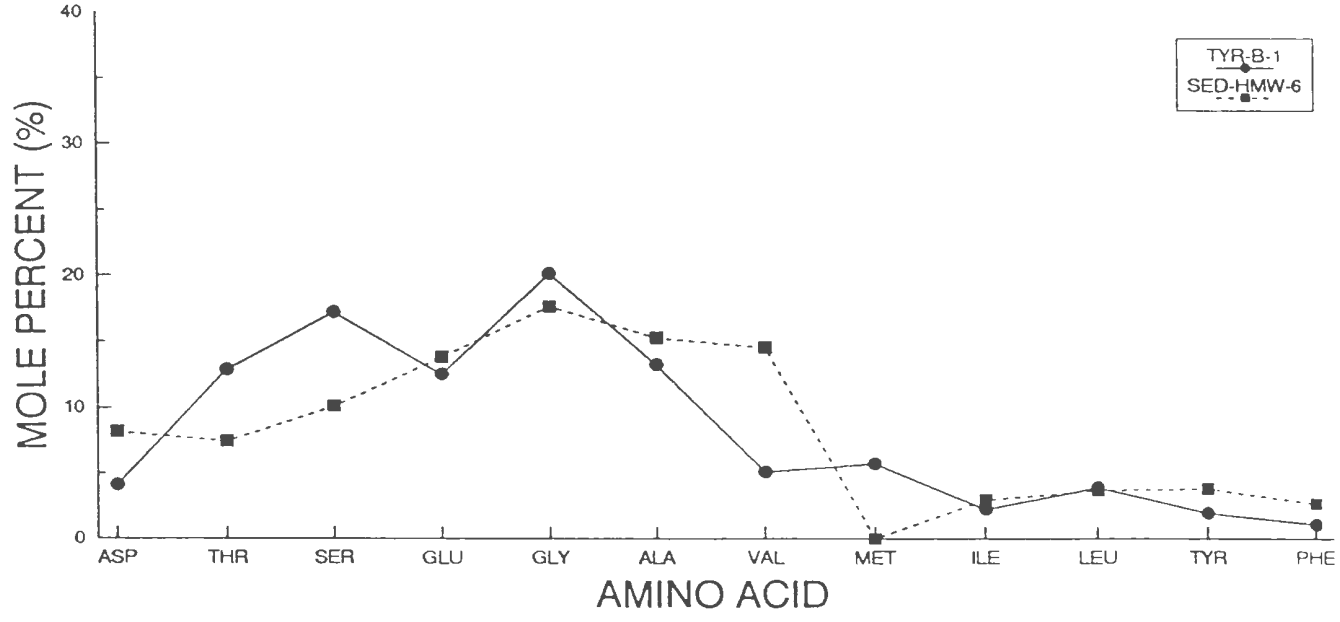

TYR-B-1
SED-HMW-6
MOLE PERCENT (%)
40
30
20
10
0
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID

Figure 18. Difference in amino acid composition (mole percent) between high molecular weight material(HMW) from five fossils and high molecular weight (HMW) material from associated sediment.

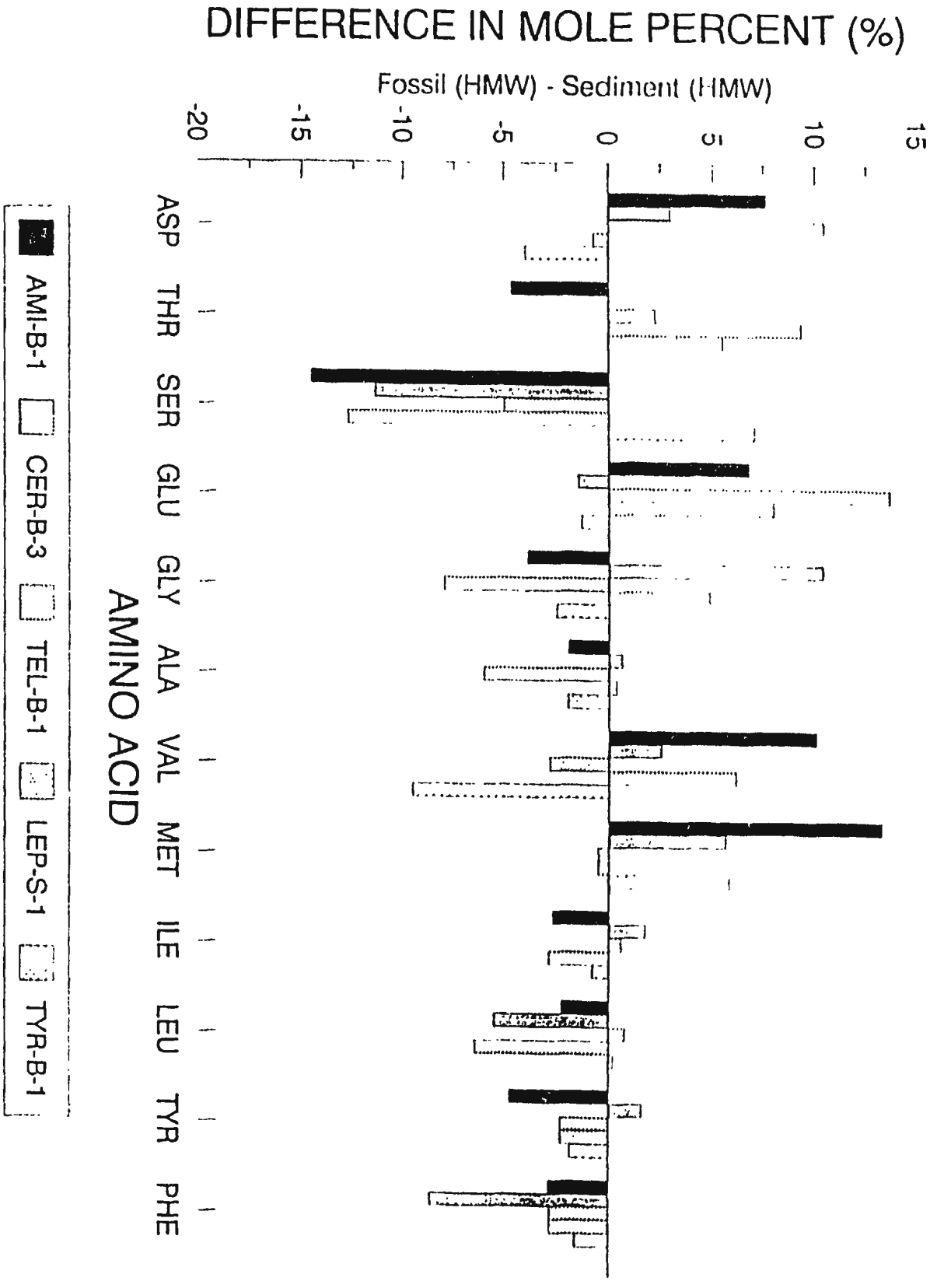

DIFFERENCE IN MOLE PERCENT (%)
Fossil (HMW) - Sediment (HMW)
-20
-15
-10
-5
0
5
10
15
ASP
THR
SER
GLU
GLY
ALA
VAL
MET
ILE
LEU
TYR
PHE
AMINO ACID
AMI-B-1
CER-B-3
TEL-B-1
LEP-S-1
TYR-B-1

Figure 19. Difference in amino acid composition (mole percent) between high molecular weight material (HMW) from a non-porous (clean) section anda porous (dirty) section of a ceratopsid bone.

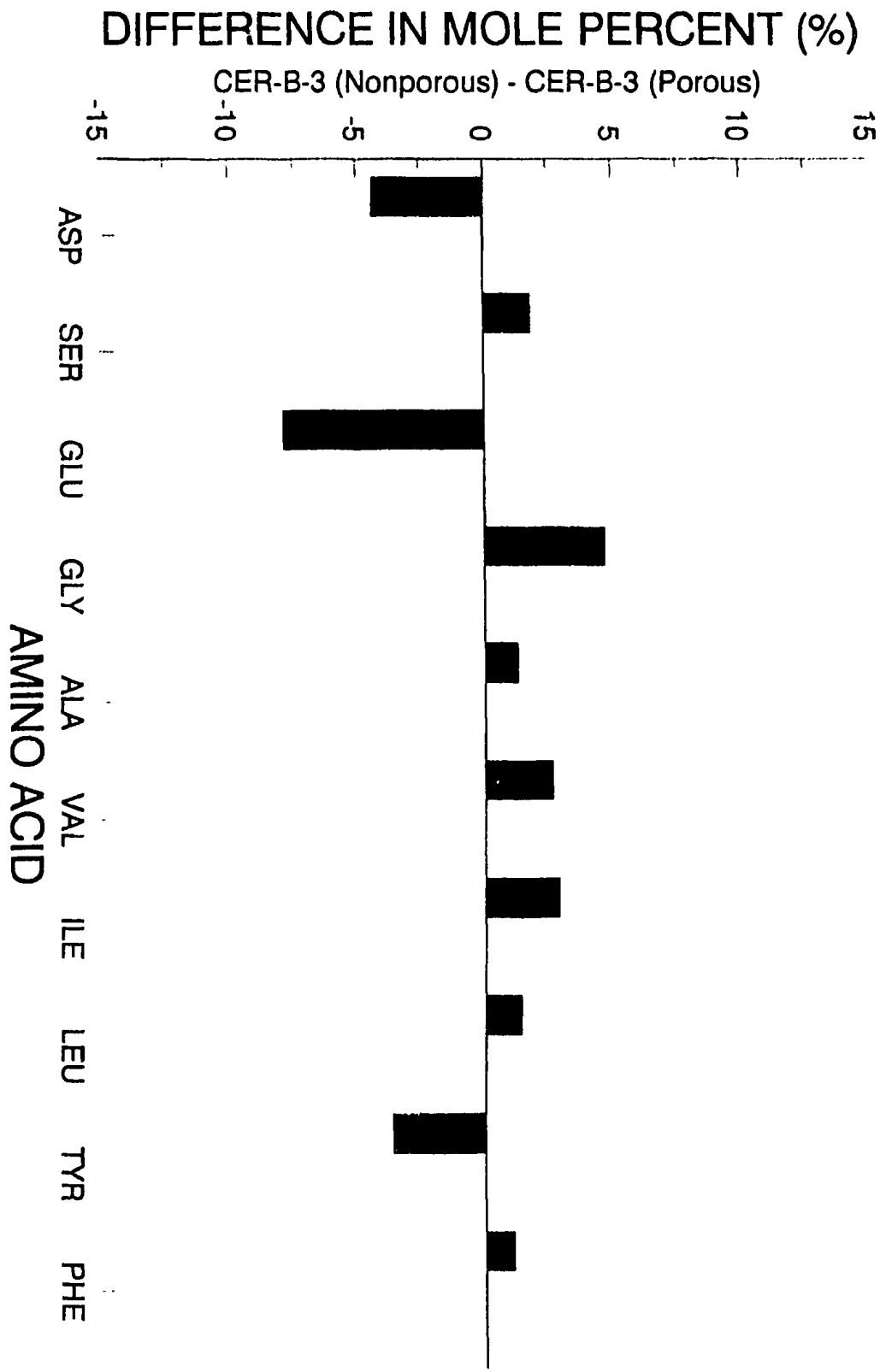
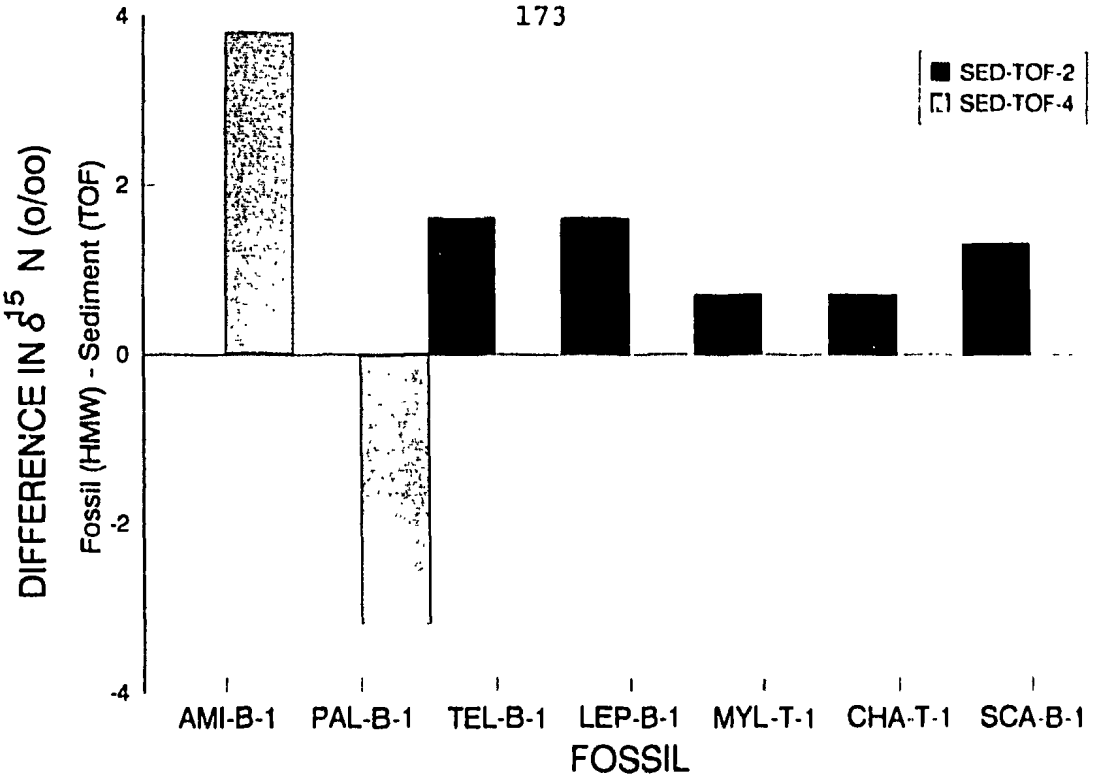

DIFFERENCE IN MOLE PERCENT (%)
CER-B-3 (Nonporous) - CER-B-3 (Porous)
-15
-10
-5
0
5
10
15
ASP
SER
GLU
GLY
ALA
VAL
ILE
LEU
TYR
PHE
AMINO ACID

Figure 20. Difference in $\delta^{15}N$ between high molecular weight (HMW) material from eight fossils and HMW material and the TOF of the associated sediment.


SED-TOF-2
SED-TOF-4
DIFFERENCE IN δ15 N (o/oo)
Fossil (HMW) - Sediment (TOF)
4
2
0
-2
-4
AMI-B-1
PAL-B-1
TEL-B-1
LEP-B-1
MYL-T-1
CHA-T-1
SCA-B-1
FOSSIL

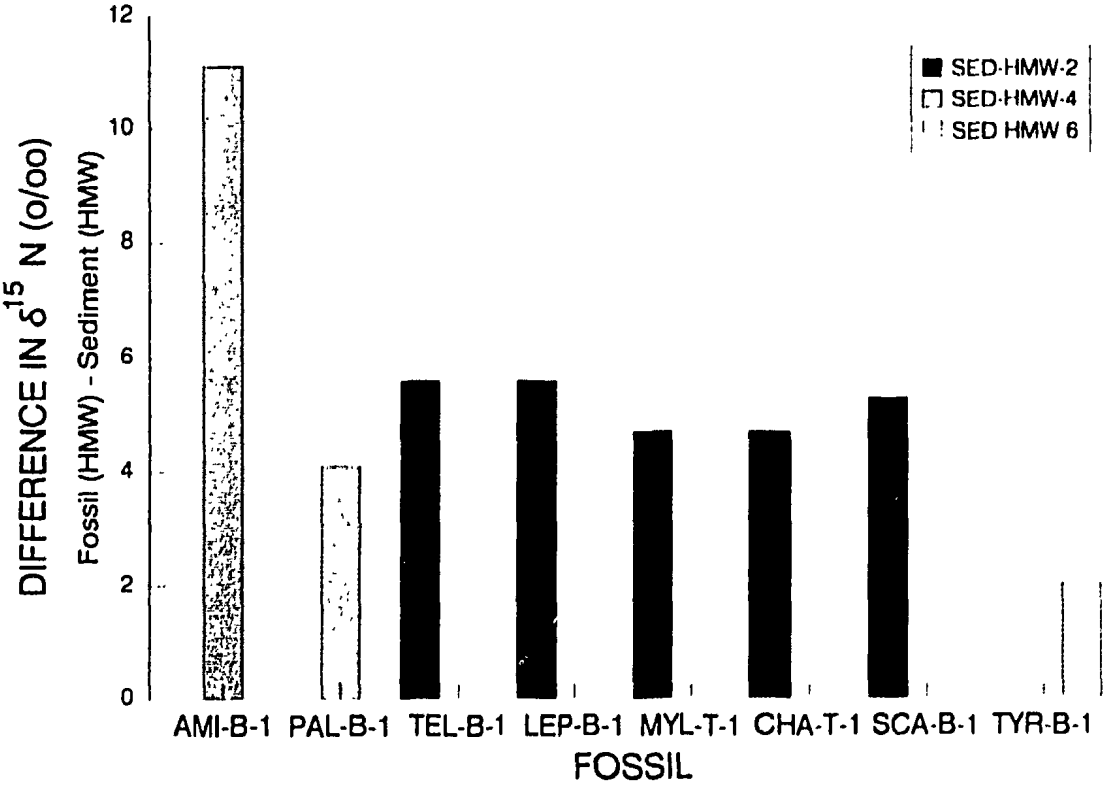

SED-HMW-2
SED-HMW-4
SED HMW 6
DIFFERENCE IN δ15 N (o/oo)
Fossil (HMW) - Sediment (HMW)
12
10
8
6
4
2
0
AMI-B-1
PAL-B-1
TEL-B-1
LEP-B-1
MYL-T-1
CHA-T-1
SCA-B-1
TYR-B-1
FOSSIL

Figure 21. Carbon and nitrogen isotopic compositions of high molecular weight material from fossils of terrestrial vertebrates.

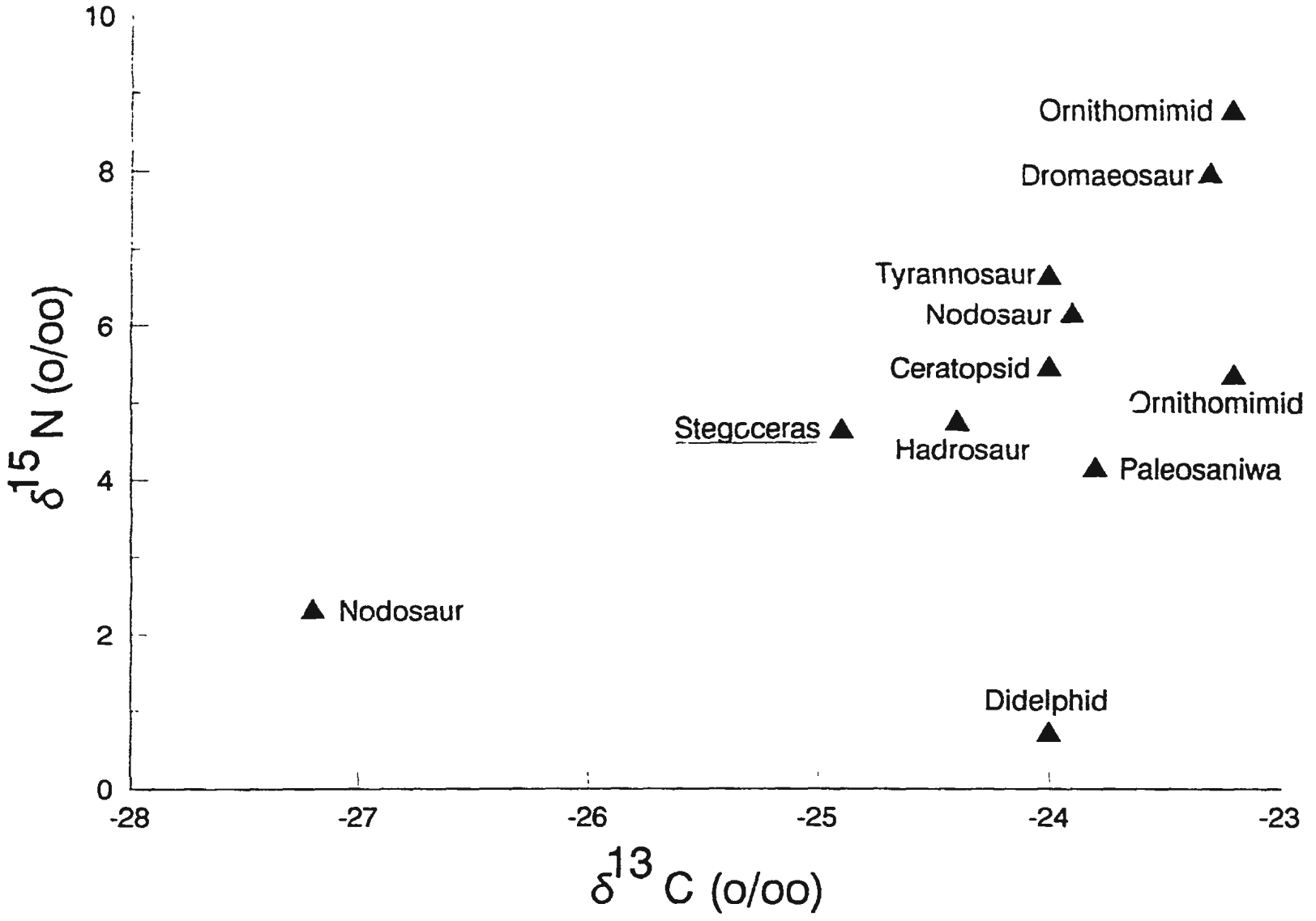

10
8
6
4
2
0
-28
-27
-26
-25
-24
-23
δ15 N (o/oo)
δ13 C (o/oo)
Ornithomimid
Dromaeosaur
Tyrannosaur
Nodosaur
Ceratopsid
Ornithomimid
Stegoceras
Hadrosaur
Paleosaniwa
Nodosaur
Didelphid

Figure 22. Carbon and nitrogen isotopic compositions of high molecular weight material from fossils of aquatic vertebrates.

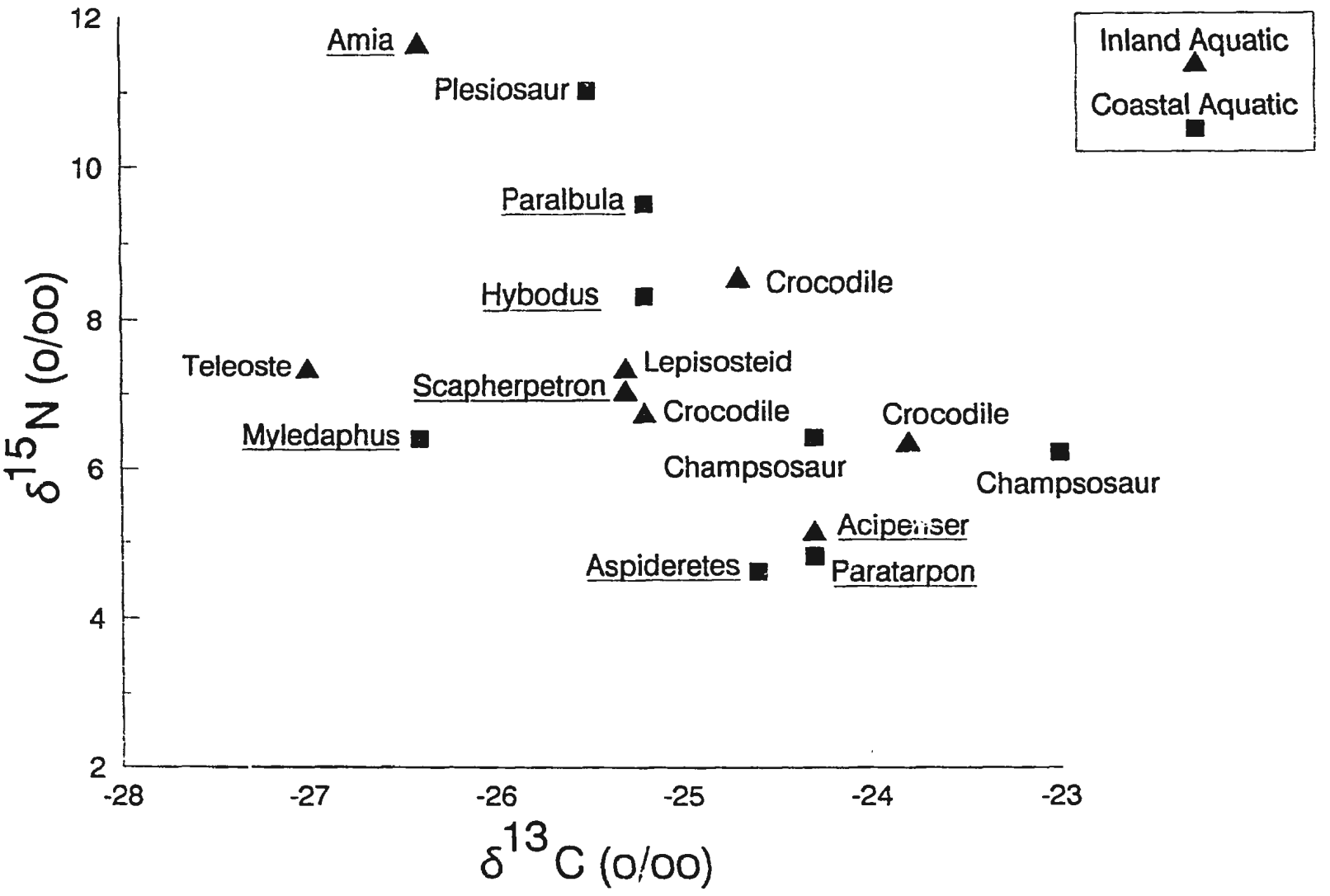
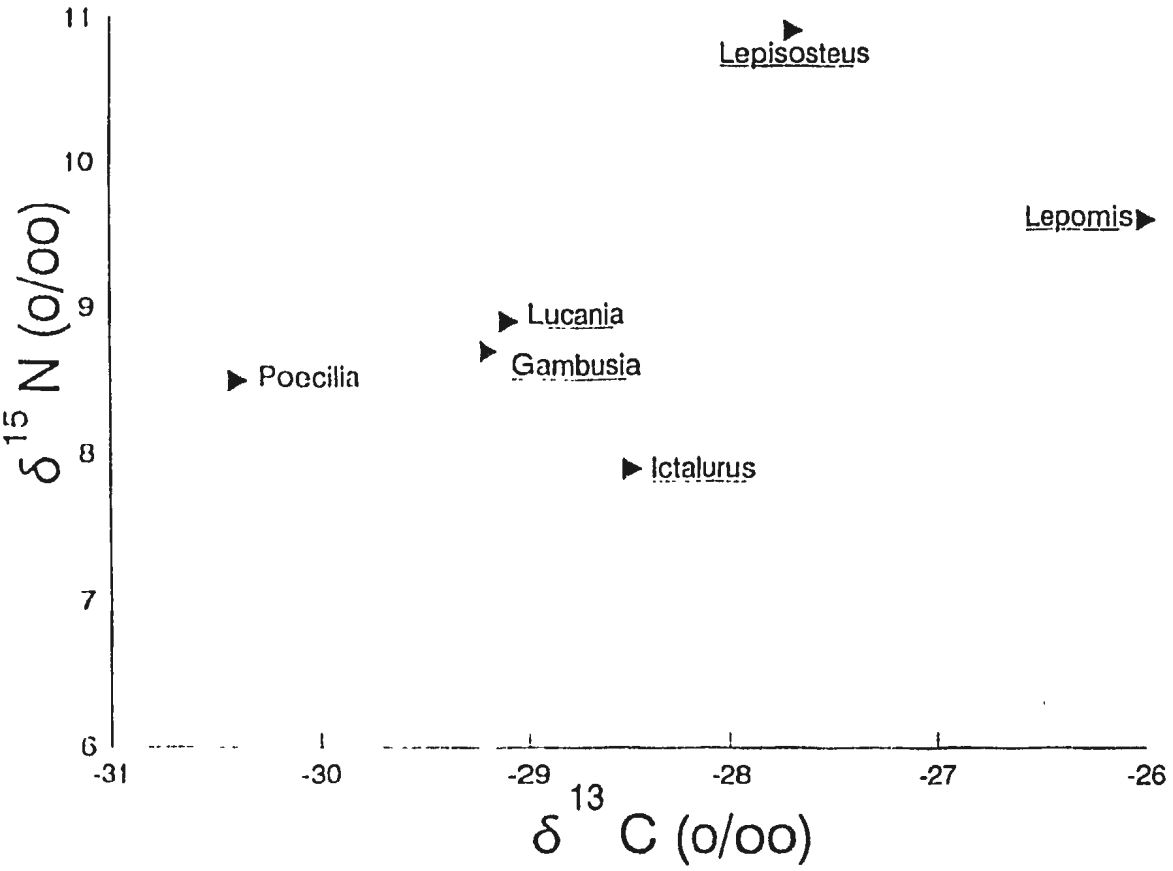

Inland Aquatic
Coastal Aquatic
Amia
Plesiosaur
Paralbula
Hybodus
Crocodile
Teleoste
Lepisosteid
Scapherpetron
Crocodile
Crocodile
Myledaphus
Champsosaur
Champsosaur
Acipenser
Aspideretes
Paratarpon
12
10
8
6
4
2
-28
-27
-26
-25
-24
-23
δ15N (o/oo)
δ13C (o/oo)

Figure 23. Carbon and nitrogen isotopic compositions of whole bodies or muscle tissue of aquatic fish from Everglades National Park, Florida (P.H. Ostrom, unpublished data).


11
10
9
8
7
6
δ 15 N (o/oo)
Lepisosteus
Lepomis
Lucania
Gambusia
Poecilia
Ictalurus
-31
-30
-29
-28
-27
-26
δ 13 C (o/oo)

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Appendix 1

Ion Fragmentation Pattern for PFP-isopropyl esters as determined by GCMS

Amino Acid	Ion Fragments (m/z)									
Ala	190	191	119	69	72	119	188	192	216	
Thr	203	202	119	57	84	189	248	204	231	230
Val	218	55	203	219	164	204	176	119	221	220
Ile	232	69	203	233	221	204	176	164	119	175
Leu	190	69	232	234	164	203	176	216	221	218
Gly	176	177	119	204	69	147	174	202	202	128
Ser	189	188	119	69	70	160	234	216	190	215
Asp	234	262	235	189	190	216	192	276	70	217
Hypro	213	67	215	119	69	68	260	259	216	215
Pro	216	217	119	69	71	214	261	146	242	189
Met	61	203	221	75	202	263	216	207	267	250
Glu	202	248	230	275	203	230	207	248	267	275
Phe	91	148	190	266	147	119	103	266	207	191
Lys	230	176	207	267	231	281	190	193	202	253
Ohlys	228	189	202	207	229	216	267	119	175	281
Phe	91	148	191	266	103	147	119	207		

Appendix 2

Taxonomy of vertebrates which appear in the results of this study (Romer, 1966; Russell, 1989; Brinkman, in press).

CLASS REPTILIA

Order Saurischia

Suborder Theropoda

Coelophysis

Infraorder Carnosauria

Family Tyrannosauridae
Albertosaurus
Tyrannosaurus

Infraorder Ornithomimosauria

Family Ornithomimidae

Infraorder Deinoychosauria

Family Dromaeosauridae
Dromaeosaurus

Order Ornithischia

Suborder Ornithopoda

Infraorder Iguanodontia

Family Hadrosauridae

Subfamily Hadrosaurinae
Kritosaurus
Prosaurolophus

Subfamily Lambeosaurinae
Corythosaurus
Lambeosaurus

Suborder Ankylosaluria

Family Nodosauridae
Nodosaurus
Panoplosaurus

Family Ankylosauridae
Euoplocephalus

Suborder Pachycephalosauria

Family Pachycephalosauridae
Stegoceras

Suborder Ceratopsia

Family Ceratopsidae

Subfamily Centrosaurinae
Centrosaurus

Subfamily Chasmosaurinae
Chasmosaurus

Order Sauropterygia

Suborder Plesiosauria

Order Chelonia

Suborder Amphichelydia

Family Baenidae

Suborder Cryptodira

Family Dermatemydidae
Dermatemys

Family Trionychidae
Aspideretes

Order Crocodilia

Suborder Eusuchia

Family Crocodilidae
Leidyosuchus

Order Choristodera

Family Champsosauridae
Champsosaurus

Order Squamata

Suborder Lacertilia

Family Varanidae
Palaeosaniwa

Family Mosasauridae

CLASS AMPHIBIA

Order Urodela

Family Scapherpetontidae
Scapherpeton

CLASS CHONDRICHTHES

Order Batoidea

Family Dasyatidae
Myledaphus

CLASS OSTEICHTHYES

Order Amiiformes

Suborder Amioidei

Family Amiidae
Amia

Order Acipenseriformes

Family Acipenseridae
Aciperser

Order Lepisosteiformes

Family Lepisosteidae

Division Teleostei

Order Elopiformes

Family Elopidae
Paratarpon

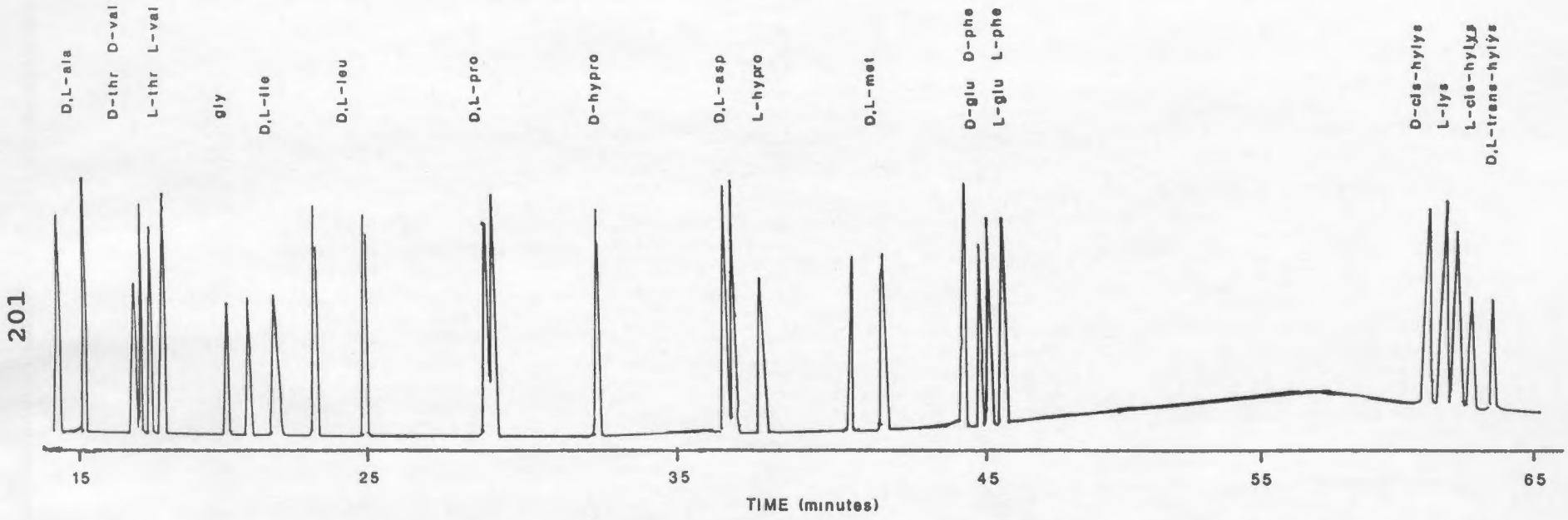
Family ?Phyllodontidae
Parabula

CLASS MAMMALIA

Order Marsupialia

Family Didelphidae

Appendix 3. Gas Chromatographic Separation of Amino Acid Enantiomers.



Appendix 4 (based on Brinkman, in press)