STABLE-ISOTOPE AND TRACE-ELEMENT GEOCHEMISTRY OF MOLLUSCAN FOSSILS FROM THE CRETACEOUS BEARPAW MARINE CYCLOTHEM OF THE WESTERN INTERIOR BASIN OF NORTH AMERICA

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Shaoneng He

Saskatoon, Saskatchewan, Canada

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ABSTRACT

The Late Cretaceous Bearpaw Formation and its equivalents (products of deposition during the last major transgressive-regressive marine cycle to affect the Western Interior Basin) contain a molluscan fauna dominated by ammonites and bivalves. Other than molluscs, representatives of the invertebrate megafaunal groups that were prevalent in the open seas and oceans are relatively rare or absent. Usually, this is attributed to brackish-water conditions or oxygen-deficient environments in the Bearpaw epicontinental sea. Investigation of stable-isotope and major- and trace-element compositions of well-preserved carbonate shells of the ammonites and bivalves from the Bearpaw cyclothem provides valuable information about environmental conditions within the Bearpaw sea.

A clear relationship exists between the $\delta^{18}O$ values of Bearpaw zonal baculitids and their biostratigraphic sequence. The baculitids from the zones denoting peak transgression have the lowest average $\delta^{18}O$ values (-2.3 to - 0.7‰), whereas those from the underlying and overlying zones have higher $\delta^{18}O$ values (-0.8 to 0.22‰). This pattern of the $\delta^{18}O$ values can only be explained by fluctuations in temperature, rather than variations in fresh-water influx, which may have been reduced due to lower precipitation and run-off under drier, warmer, climatic conditions. Inoceramids usually have the highest $\delta^{13}C$ values (0.6 to 5.0 ‰) and lowest $\delta^{18}O$ values (-4.0 to -2.8 ‰), whereas coeval baculitids have the lowest $\delta^{13}C$ values (-4.8 to -0.3‰) and the highest $\delta^{18}O$ values (-2.3 to 0.0 ‰). The large differences in stable-isotope values imply that these animals must have inhabited isotopically distinct reservoirs within the Bearpaw sea. Thus, the baculitids probably hovered and swam mostly in the upper part of the water column in contrast to the inoceramids which are known to have been benthonic. *Didymoceras*, with isotopic compositions similar to those of benthonic inoceramids, also probably lived very close to the bottom. The heterogeneity of the stable-isotope compositions of these coeval benthonic and nektonic molluscs points to isotopically distinct, stratified, reservoirs within the seaway, much like those inferred for the older Claggett and Greenhorn seas. Causes of this stratification may have involved modification of bottom water through isotopic exchange reactions between the water and the sediments near or at the bottom of the sea.

Relatively constant element/Ca ratios of nektonic baculitids indicate a stable chemical composition for the upper water column of the seaway. This suggests a low fresh-water influx, as indicated also by the stable-isotope compositions. Benthonic fossils have more variable compositions due partly to modification by pore waters derived from the sediments. Both nektonic and benthonic molluscs exhibit relatively high Ce/Ce* values (-0.16 to 0.02), similar to the seawater in anoxic and dysoxic environments of modern oceans and seas. Therefore, the seaway was probably dysoxic in both its upper and bottom waters through most of the Bearpaw cycle. Low oxygen-level conditions are reflected by characteristics of the Bearpaw sedimentary rocks and fauna in general. With the seeming absence of brackish waters, dysoxia may account for the rarity of other normal, open ocean, invertebrate organisms.

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Dr. W.A. Cobban of the United States Geological Survey kindly and generously permitted use of his collection of molluscan fossils from the Bearpaw and equivalent formations in the United States, and Dr. T.E. Bolton of the Geological Survey of Canada, Ottawa, allowed me to sample similar molluscs from Canada, collected in the past by that Survey's officers.

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1. INTRODUCTION

1.1 The Cretaceous Western Interior Basin

The Cretaceous Period was an important one in the geological history of the Western Interior of North America, during which the region was the site of one of the largest foreland basins in the world, extending from the Gulf of Mexico northward to the Arctic Ocean and from eastern British Columbia to western Ontario (Fig.1.1). The basin was bounded on the west by the mountainous, narrow, and unstable proto-Cordillera which extended from central America to Alaska and separated the basin from the Pacific Ocean. On the east, the basin was bounded by the low-lying stable Craton of North America.

The Western Interior foreland basin formed between the Middle Jurassic and Early Tertiary times as a result of flexural subsidence due to thrust sheet-loading related to major collisional events on the western continental margin (Beaumont *et al.*, 1993). These tectonic events provided a source of detritus in the proto-Cordillera, a gradient to transport sediment eastward, and a basin in which to deposit it. The Western Interior Basin itself was composed of a series of elongate tectonic zones: the western foredeep, west-median trough, east-median hinge, and eastern platform (Fig.1.2). These zones rose and subsided differentially, yet generally synchronously, in response to deformational events in the proto-Cordillera and the subsequent direct and indirect effects on the crust and mantle beneath the basin (Kauffman and Caldwell, 1993).

Fig.1.1 Map showing the extent of the Cretaceous Western Interior Seaway of North America during the Bearpaw marine cyclothem (*Baculites baculus* time). After Williams and Stelck (1975).

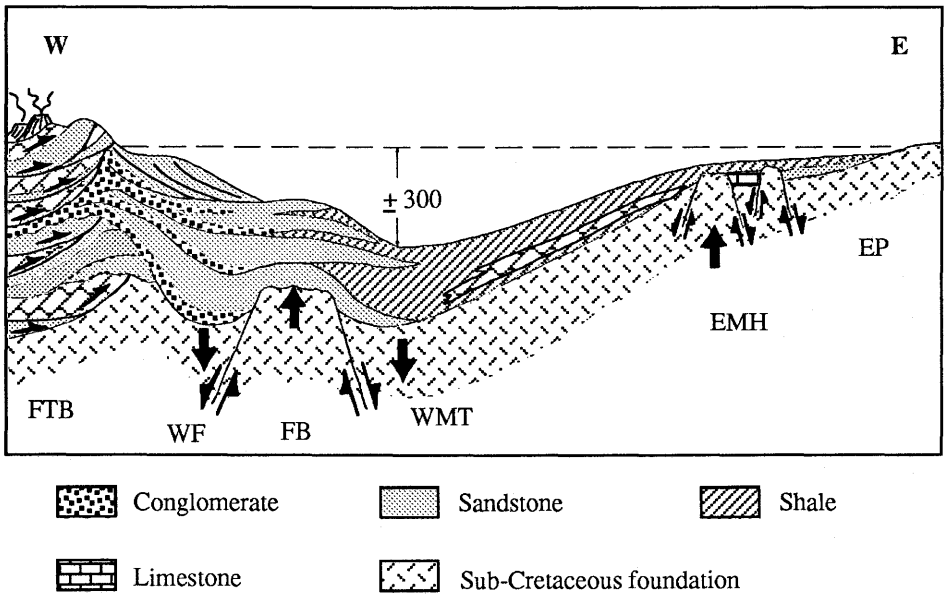


Fig. 1.2 Distribution of tectonic zones in the Cretaceous Western Interior Basin of North America. FTB: Cordilleran fold-and thrust belt; WF: western foredeep; FB: foreland buldge; WMT: west-median through, characterized by greatest water depths (shown in meters); EMH: east-median hinge between the stable platform to the east and the west-median through to the west; EP: eastern platform. Modified after Kauffman (1988) and Cadrin (1992).

There were ten major transgressive-regressive (T-R) marine cycles around the world during the Cretaceous Period (Kauffman, 1977). Four of these cycles (the Greenhorn, Niobrara, Claggett, and Bearpaw), which took place during the Late Cretaceous Epoch, are recorded by the sedimentary rocks in the Western Interior Basin (Fig. 1.3). Initial inundation occurred only in the north during the Early Cretaceous Epoch, and proceeded through a series of progressively southward incursions until early Late Albian time, when initial connection with the southern arm of the seaway was temporarily established. During much of the period between the Albian and Maastrichtian ages, the Western Interior Seaway linked circum-polar and subtropical seas.

The paleoenvironment of the Cretaceous Western Interior Seaway is essential to understanding the geological development of North America in later Mesozoic time. As such, the seaway has been the subject of numerous investigations, including geochemical studies by Tourtelot (1962, 1964), Tourtelot and Rye (1969), Forester *et al.* (1977), Wright (1987), Whittaker *et al.* (1987), Kyser *et al.* (1993), and Whittaker and Kyser (1993). The main objective of the research being described herein is to contribute to that paleoenvironmental knowledge through a study of the molluscan fossils from the Bearpaw cyclothem, the last major T-R cycle, Late Campanian to late Early Maastrichtian in age, using stable-isotope and major- and trace-element distributions. This study contributes important information on the paleoenvironmental conditions of deposition of the Bearpaw sediments and their equivalents. The fossils used are mainly from localities in the central portion of the Western Interior Basin, an area where sediments and fossils record the meeting and mixing of waters from the two

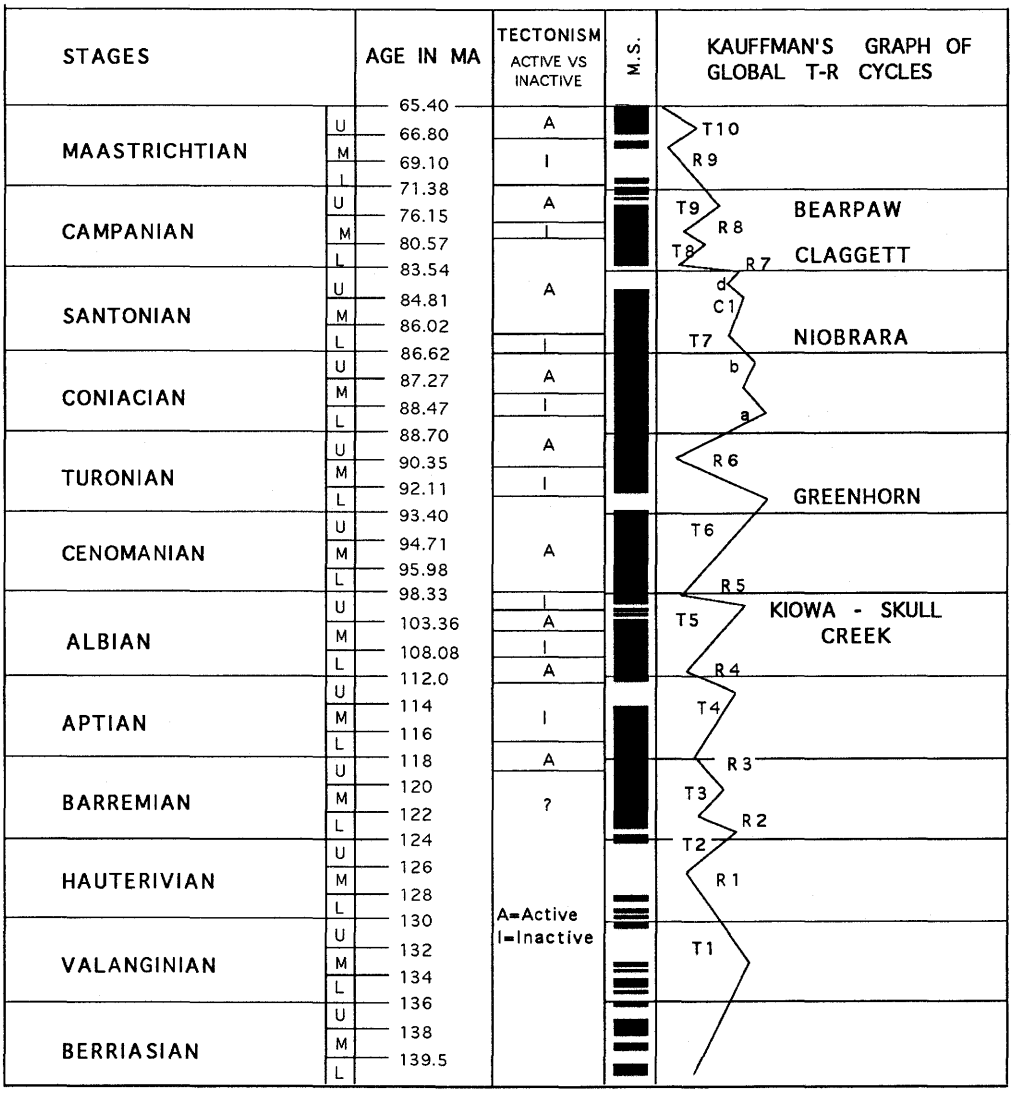


Fig. 1.3 Summary chart for the Cretaceous Western Interior Basin of North America showing (from left to right column): a general comparison of Cretaceous stage divisions with the new radiometric time scale of Obradovich (1993); alternating, tectonically and vocanically active (A) intervals, and relatively inactive (I) intervals (tectonic quiescence) in the Cretaceous Western Interior Basin of North America, based on collective data; magnetostratigraphy (M.S.); and the ten eustatically controlled, transgressive-regressive, marine cycles. Modified after Kauffman and Caldwell (1993) and Caldwell *et al.* (1993).

different, widely separated oceanic bodies, the Tethyan Sea from the Gulf of Mexico and the Boreal Sea from the circum-polar ocean.

1.2 Geochemistry and Paleoenvironments of the Basin

Geochemistry is a widely used method for studying paleoenvironments. If a mineral is precipitated in isotopic equilibrium with ambient water, its stable-isotope composition will be a function of the temperature, salinity, and stable-isotope composition of the water (Milliman *et al.*, 1974). Chemical composition of a mineral deposited in the sea is also directly and indirectly controlled by chemical and physical conditions of the seawater (Lorens and Bender, 1980; Boyle and Keigwin, 1985/86; Wright *et al.*, 1984; David and Boyle, 1993). Investigation into stable isotopic and chemical compositions of minerals (e.g., fossils shells) precipitated in sedimentary environments, in combination with petrology and paleontology, can provide quantitative information about paleoenvironmental conditions of ancient oceans and seas.

Stable-isotope and trace-element geochemical methods have long been utilized to trace the paleoenvironmental conditions of the Western Interior Basin. The research by Lowenstam and Epstein (1954) was the earliest attempt to explore the paleoenvironment of the basin using the stable-isotope compositions of molluscan fossils. Their results indicated a progressive rise in the temperatures of the Late Cretaceous oceans and seas from the Cenomanian, climaxing in Coniacian-Santonian times, followed by a general decline to Maastrichtian time. Since this preliminary work, many studies have investigated the chemical and isotopic compositions of sedimentary rocks and fossils from the basin (e.g., Tourtelot, 1962, 1964; Tourtelot and Rye, 1969; Scholle and

Kauffman, 1975; Kauffman, 1977, 1988; Wright, 1987; Whittaker *et al.*, 1987; Arthur *et al.*, 1985, 1988; Pratt *et al.*, 1985, 1993; Kyser *et al.* 1993; Whittaker and Kyser, 1993; Cadrin *et al.*, 1996). These latter studies provided deeper insights into the paleoclimate and paleo-oceanography of the seaway during the Late Cretaceous Epoch. Due to the importance of these studies to this research, a brief synopsis of the principal collective findings of these investigations follows.

Most of the previous geochemical studies of the basin focused on the two most complete and widely traceable transgressive-regressive sequences, namely the Greenhorn and Niobrara marine cyclothems, because they encompass the more important Cretaceous extinction events and global oceanic anoxic events (OAEs). Significant variations in the $\delta^{13}C$ values of organic matter and $\delta^{13}C$ and $\delta^{18}O$ values occur in Cenomanian-Turonian rocks and fossils basin-wide (Pratt, 1983; Cadrin, 1992; Pratt *et al.* 1993). These fluctuations are notable because of their association with a global second-order mass-extinction event at the Cenomanian-Turonian boundary, and a global OAE (the Bonarelli event) at peak transgression of the Greenhorn sea just prior to this boundary (Pratt, 1985; Orth *et al.*, 1988; Cadrin, 1992). Lithologic cycles of limestone-marl bedding couplets of the Greenhorn and Niobrara formations are well characterized by the cyclic fluctuations in $\delta^{18}O$ and $\delta^{13}C$ values of carbonates and $\delta^{13}C$ values of organic matter across individual limestone and marl couplets throughout the basin (Pratt, 1983; Cadrin, 1992; Pratt *et al.*, 1993). The fluctuations are interpreted as a primary signal of shifts in regional climate related to Milankovitch-scale insolation alternations (Pratt *et al.*, 1993), which affected salinity of the surface water through freshwater influx into the seaway from the emerging Rocky Mountains. During wet periods, high

freshwater influx caused salinity stratification in the water column and stagnation of the bottom water. This is expressed in clastic-rich deposits with high organic-carbon contents, high $\delta^{13}C$ values, and low $\delta^{18}O$ values. In dry periods, vertical mixing of the water column occurred, which is depicted in carbonate-rich deposits with low organic-carbon contents, moderate $\delta^{13}C$ values, and less negative $\delta^{18}O$ values. Furthermore, variations in the stable-isotope compositions of carbonates and organic carbon have been proposed as the chemostratigraphic marker of the Cretaceous System in the Western Interior Basin (Arthur *et al.*, 1985; Kauffman, 1988; Cadrin, 1992).

A few studies have dealt with the geochemistry of the younger Claggett and Bearpaw cyclothems. After Lowenstam and Epstein (1954), Tourtelot and Rye (1969) began a systematic investigation of the stable-isotope compositions of molluscs from the Upper Cretaceous (Campanian and Maastrichtian) Pierre Shale in the United States. They found that inoceramids generally had much lower $\delta^{18}O$ values than coexisting ammonites, and proposed that the inoceramids exhibited metabolic fractionation ("vital effect") and, therefore, that their isotopic compositions could not be used as a paleoenvironmental indicator. However, Rye and Sommer (1980) indicated that the lower $\delta^{18}O$ values of the inoceramids are not due to "vital effect" but essentially record original paleoenvironmental conditions. Forester *et al.* (1977) examined the stable-isotope compositions of ammonites and bivalves from the Bearpaw Formation in Saskatchewan. Their work was the first systematic study of isotope geochemistry of molluscan fossils constrained in terms of both geographical area and bisotratigraphic section of sequential ammonite zones. Whittaker *et al.* (1987) discovered anomalously high concentrations of magnesium (Mg) in molluscan shells from specific strata of the

Claggett Formation. The Mg-enriched fossils constitute an inferred chronostratigraphic marker which can be traced from southern Saskatchewan to the mid-western United States. The investigations discussed above reported significant differences in the stable-isotope compositions of molluscan fossils from the Claggett and Bearpaw cyclothems in both the Canadian and American portions of the basin, although the coeval sedimentary rocks and faunal assemblages generally do not contain evidence of any notable extinction events or OAEs. These variations have been explained by isotopic stratification of the seaway (Wright, 1987; Whittaker *et al.*, 1987; Kyser *et al.*, 1993). Trace-element geochemical methods, which can provide information on paleoenvironments as indicated by Calvert and Pederson (1993), and Whittaker and Kyser(1993), have not yet been systemically applied to the Bearpaw Formation and its equivalents.

1.3 Some Outstanding Problems

1.3.1 Paleoenvironments of the Bearpaw Sea

Difficulty in determining the paleoenvironments of the Western Interior Seaway arises partially from the fact that the fauna is dominated by ammonites and bivalves and lacks many of the taxa that typically prevailed in the contemporaneous open oceans and seas, including most echinoderms, corals, bryozoans, brachiopods, and skeletonized sponges (Gill and Cobban, 1966; Caldwell, 1968; Kauffman and Caldwell, 1993). This characteristic of the faunas is usually attributed to the existence of dysoxic to anoxic mid- to bottom-water environments through much of the basin's history. Such environments supported relatively abundant, opportunistic, low oxygen-adapted taxa (Kauffman and Sageman, 1990; Kauffman and Caldwell, 1993). Periodical and long-

lived dysoxic to anoxic environments of the seaway have also been invoked to account for the accumulation of organic-rich sediments within the seaway (Kauffman and Caldwell, 1993).

Dysoxic to anoxic mid- to bottom-water environments have been attributed to water-mass stratification in the seaway through much of the Late Cretaceous Epoch caused by interaction of the different transgressive seas. Kauffman (1975, 1988) suggested a horizontal to low-angle stratification of less dense, normal saline to slightly brackish waters derived from the proto-Gulf of Mexico over colder, possibly slightly brackish waters of greater density derived from the northern circum-polar ocean. Salinity stratification was enhanced during peak transgressions by internal freshwater run-off into the basin, or by northward incursions of an expanded oxygen-minimum zone from the proto-Gulf of Mexico and Caribbean region (Kauffman, 1988). This stratification diminished downward-mixing of oxygenated surface waters, thereby reducing benthonic oxygenation. Dysoxic to anoxic conditions resulted, with enhanced accumulation of organic carbon in the sediments.

Hay *et al.* (1993) proposed a different model to explain dysoxic-anoxic conditions and organic-carbon accumulation in the Western Interior Basin. They suggested that the water masses from different regions may have had similar densities but very different salinities and temperatures, as in the case of the modern waters of the Gulf of Mexico and eastern Arctic Ocean. Mixing of two such water masses would produce a blended water mass of greater density than either the northern or southern components which would rapidly sink to the sea floor as a downwelling zone. As it did so, it would carry large quantities of organic material with it, which would saturate the low water

column with organic material and rapidly deplete existing oxygen.

Recent data collected from high-resolution biostratigraphic and lithostratigraphic analyses of organic-rich black shales in the basin (Kauffman and Sageman, 1990; Davis and Byers, 1993) have raised serious questions about persistent density stratification as a cause of long-lived anoxia and organic-carbon accumulation in the Late Cretaceous Epoch. These data show that, even during major incursions of oxygen-depleted waters into the basin during the Cenomanian-Campanian ages, benthonic conditions were highly dynamic. The bottom of the seaway was frequently oxygenated by bottom currents, major storm and mass-flow events and changes in water-mass stratification associated with Milankovitch climatic cyclicity. Studies of modern marine sediments (Jorgensen, 1982; Calvert, 1990; Pedersen and Calvert, 1990; Calvert and Pedersen, 1992) suggested that high primary production of organisms -- *not* water-column anoxia -- provided the first-order control on the accumulation of organic-rich facies in modern oceans. Lack of oxygen does not appear to have a direct effect on organic-carbon accumulation in continental-margin or marginal-sea environments. Sediments accumulating in the modern Black Sea -- the type anoxic basin -- are not particularly enriched in organic matter, and a sapropel containing extremely high carbon concentrations was deposited during the Holocene Epoch at a time when the basin was oxic (Calvert, 1990). Thus, long-term dysoxic to anoxic environmental conditions may not be the cause of a high preservation rate of organic carbon, or of the scarcity of larger normal marine animals other than ammonites and bivalves in the Western Interior Basin during the Late Cretaceous Epoch.

The prevalence of somewhat brackish-water conditions in both surface and

bottom waters in the seaway during the Late Cretaceous Epoch offers another possible explanation for the character of the faunas (Kauffman and Caldwell, 1993). Due to the influx of freshwater, especially during wet Milankovitch climatic hemicycles and even in shallow, fully oxygenated waters, biotas are of sub-normal marine diversity and lack many typical marine faunal representatives. Brackish surface waters could greatly affect biological diversity and representation in the Western Interior Basin through exclusion of, or reduction in, the salinity-sensitive planktotrophic larvae of benthonic marine organisms. Isotopic studies of Late Cretaceous sedimentary rocks and fossils from the basin (Cadrin, 1992; Kyser *et al.*, 1993; Pratt *et al.*, 1993) indicated somewhat more negative $\delta^{18}O$ values than those of normal open-marine water. This may suggest the existence of brackish-water in the seaway. However, more negative $\delta^{18}O$ values of the water could also imply higher average temperatures for the seaway than for coeval open oceans and seas. Therefore, variations in the $\delta^{18}O$ values of molluscs from the seaway could be due to more than one possible variable.

On the basis of geochemical and sedimentary studies of the Greenhorn and Niobrara formations, Pratt (1985), Arthur *et al.*(1985), Barron *et al.* (1985), and Pratt *et al.* (1993) developed a model in which variations between wet and dry climates are reflected in the cyclicity of sediments from the seaway. This model is based on the fluctuations in the carbon- and oxygen-isotope compositions of rocks and organic carbon isotopic compositions through time. The model does not, however, explain the stable isotopic patterns exhibited by fossils from such younger formations as the Claggett and Bearpaw. The investigations by Tourtelot and Rye (1969), Forester *et al.* (1977), Wright (1987), Whittaker *et al.* (1987), and Whittaker (1989) showed that significant

differences usually exist in the stable-isotope compositions of coexisting ammonite and bivalve shells. In fact, the stable-isotope compositions of these fossil seems to suggest an isotopic stratification of the Greenhorn, Claggett, and Bearpaw seas wherein the bottom waters have lower $\delta^{18}O$ values than those above. These studies provided explanations for variations in oxygen, but not the carbon, isotopic compositions of the fossils. Hence, it is becoming increasingly evident that, before the precise mechanism producing the apparent stable isotopic stratification is resolved and refined, the nature of the water masses in the seaway must be well understood through basin-wide investigation of stable-isotope compositions and trace-element contents of minerals precipitated from various portions of the seaway.

1.3.2 Mode of life of ammonites

The mode of life of Mesozoic ammonoids has been a topic of inquiry for over a century, but one severely hampered by the lack of living ammonoid species for comparison. The closest living analogue to the Mesozoic ammonoids is the Indo-Pacific cephalopod *Nautilus*, the only surviving member of the Nautiloidea and of the externally shelled cephalopods. Much of what is inferred about the mode of life of ammonoids, therefore, has come from comparative anatomy, shell morphology, and hydrostatic examination and hydrodynamic experiments (House and Senior, 1981; Lehmann, 1981; Saunders and Shapiro, 1986). Ammonites are thought to have been nektonic, planktonic, or nektobenthonic animals, and to have moved in a fashion very similar to modern *Nautilus*. As in *Nautilus*, the external shell not only provided protection to the soft parts, but perhaps more importantly served as a buoyancy controlling device.

Studies on the muscular markings and hydrodynamic properties of the shell (Kennedy and Cobban, 1976; Ward, 1986) suggested, however, that the majority of ammonoid species were relatively slow, weak swimmers, perhaps adapted for slow vertical excursions rather than rapid horizontal movement.

Based on the observation that the large number of species were restricted to tiny areas, Lehmann (1981) suggested a largely bottom-dwelling lifestyle for most Mesozoic ammonites. Furthermore, he thought that the peculiar shovel-like form of their lower jaws would probably be most effective just above the sea floor. The most recent study by Ebel (1992) implied that probably all ammonites were benthonic animals. His new calculations showed that normally coiled ammonoids would have needed a body chamber length of less than 180 degrees of rotation to meet all the requirements of swimming, much like the present-day *Nautilus*. As ammonoids exhibit body chambers ranging from less than 180^0 to more than 500^0 of rotation, they were probably too heavy to be strong swimmers. In addition, the assumption of a floating or swimming mode of life cannot explain the formation of three-dimensional decoiled heteromorphs. Ebel (1992) postulated that the morphology of ammonites can only be explained satisfactorily if a benthonic mode of life is assumed, and that this applies to both heteromorph and regular shells.

Appreciating the mode of life of ammonites is very important; if they were planktonic or nektonic animals, they would provide information about middle to upper water column conditions, whereas if they were benthonic animals, they would furnish information about bottom environments. This has already been demonstrated in geochemical studies of foraminifera, in which the $\delta^{18}O$ values reflect paleotemperatures

and paleocirculation (Savin, 1982). However, the mode of life of ammonites is simply assumed to be nektonic or planktonic or is ignored in many investigations of the stable isotopic and chemical compositions of their shells. In this study, the mode of life of the ammonites from the Bearpaw cyclothem will be considered carefully. Baculitids, scaphitids, and other ammonites, which are major fossils of the Bearpaw Formation and its equivalents, have been collected. Their stable-isotope compositions will be compared to those of the coexisting inoceramids which are known to have been benthonic animals. The mode of life of these ammonites will be inferred by combining these geochemical data with the results of pre-existing paleontological and hydrodynamic studies.

1.3.3. Summary of the problems

According to the above discussion, the following puzzles need to be resolved to achieve a better understanding of the development of the Cretaceous Western Interior Seaway: (1) the level of salinity of the waters within the seaway during the Late Cretaceous Epoch; (2) the degree of oxygenation of the waters within the seaway during the Late Cretaceous Epoch; (3) the cause of isotopic stratification of the waters within the seaway throughout the Late Cretaceous Epoch; and (4) the mode of life of the ammonites which lived in the seaway. Trying to solve these problems lies behind much of the research now to be described.

2. THE BEARPAW CYCLOTHEM

2.1 Lithostratigraphy and Facies Patterns

The Bearpaw marine cyclothem is represented primarily by the Bearpaw Formation (Fig. 2.1), which outcrops in southwestern Saskatchewan and southern Alberta (Furnival, 1946; Lines, 1963; Caldwell, 1968; Rask,1969), and by the Bearpaw Shale in Montana and north-central Wyoming (Tourtelot, 1962; Gill and Cobban, 1973). The formation is equal to the middle to upper part of the Pierre Shale in eastern Saskatchewan, Manitoba, and the northeastern part of the basin in the United States (Caldwell, 1968; Gill and Cobban, 1966 and 1973; McNeil and Caldwell, 1981).

The Bearpaw Formation and its equivalents form a westward-thinning cyclic wedge of predominately marine silty clays and sands, underlain by a complementary eastward-thinning wedge of predominately non-marine sands, silts, and clays of the Judith River Formation and overlain by a similar wedge formed by the Eastend and Whitemud formations in Canada, and the Fox Hills Sandstone and Hell Creek Formation in the United States (Caldwell, 1968; Gill and Cobban, 1973; North and Caldwell, 1975). Influenced by tectonic events in the flanking orogen, the western foredeep and the west-median trough of the Interior Basin underwent the greater subsidence and received the coarser-grained terrigenous clastic sediments in greater thicknesses. In the eastern part -- the east-median hinge and eastern platform of the basin -- the thinner, mainly finer-grained residues of sedimentary bypass accumulated, supplemented in small measure by

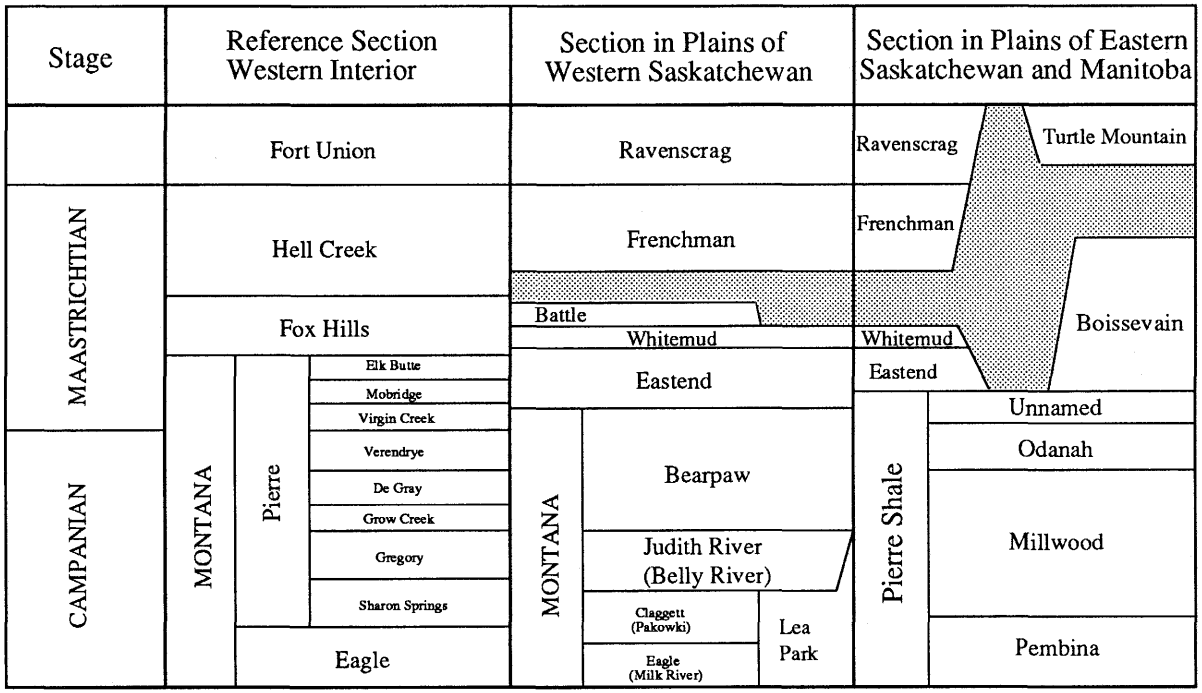


Fig. 2.1 Correlation chart of the Upper Cretaceous formations in the study area. Modified from North and Caldwell (1975), and McNeil and Caldwell (1981).

some terrigenous clastic detritus from the Craton, and by basin-generated carbonates. Calcareous shales are also common in the eastern part of the basin.

The sedimentary rocks in the Cretaceous Western Interior Basin can be simply divided into three broad facies (Fig. 2.2), which reflect a relatively simple structure of the basin during the Late Cretaceous Epoch: (1) coarse- to fine-grained sandstone facies to the west ; (2) shale, chalk, and limestone facies to the east; and (3) between them, an intervening facies with elements of both eastern and western facies. The facies belts, however, were not static. Under the influence of tectonoeustatic changes and of orogenic and epeirogenic movements, sea levels fluctuated, and the basin expanded and shrank as its flanking shorelines migrated east and west, away from and towards, the mid-line. As the shorelines migrated, so did the facies that paralleled them, resulting in the consistent positions of the facies belts relative to those that border them.

2.2 Character of the Fauna and the Biostratigraphy

2.2.1 The Bearpaw fauna

Like the older Greenhorn, Niobrara, and Claggett formations, the Bearpaw Formation and its equivalents contain a rich fauna of marine organisms, dominated by bivalves and cephalopods, but one which is poor in other normal marine animals, such as sponges, corals, brachiopods, bryozoans, and echinoderms (Gill and Cobban, 1966; Caldwell, 1968; Kauffman and Caldwell, 1993). As well, the Bearpaw fauna differs somewhat from those of these older formations which completely lack these non-molluscan organisms: Cheilostomate bryozoans exist at many levels of the Pierre Shale in the United States and in the Bearpaw Formation in the South Saskatchewan River

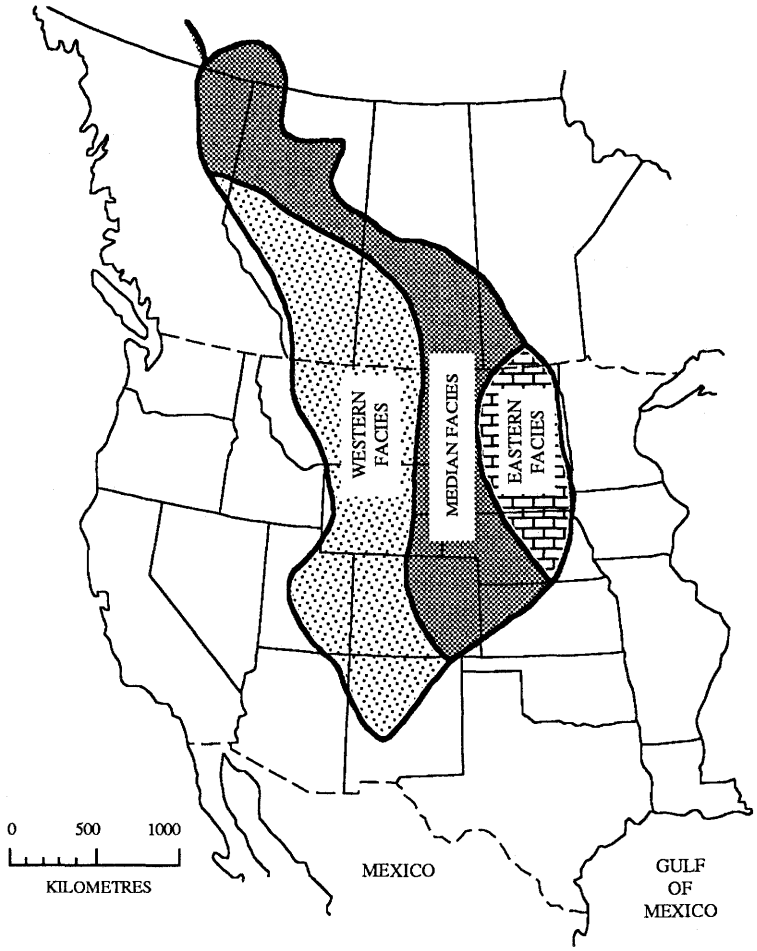


Fig. 2.2 Generalized facies belts of the Late Cretaceous rocks in the Western Interior Basin of North America. After McNeil and Caldwell (1981).

valley (Gill and Cobban, 1966; Caldwell, 1968). Corals, boring sponges, calcareous worms of various kinds, and shrimp and lobster parts are found at several localities in the basin, both in the United States and Canada. Caldwell and Evans (1963) also reported a rudistid bivalve from the South Saskatchewan River valley.

In general, the marine biota of the Western Interior Seaway was derived from three sources (Fig. 2.3; Kauffman, 1975, 1984): first, a component characteristic of the northern cool- to mild-temperate arm of the sea, which at its maximum extent reached as far south as southern Colorado; second, a component characteristic of the southern warm-temperate to subtropical arm of the sea, which extended for variable distances northward from the proto-Gulf of Mexico and Caribbean Sea; and third, a component from the broad paleobiogeographic ecotone, up to several hundred kilometers in north-south dimension, where the northern and southern arms of the seaway overlapped. High levels of endemism among the molluscs (especially ammonites) characterized this ecotone. The paleobiogeographic divisions of the seaway were not stable, however: subprovincial boundaries migrated north and south over hundreds of kilometers within short (<0.5 - 1 m.y.) time intervals. This was mainly associated with tectonoeustatic changes in sea level (Kauffman, 1984) and is most evident in the repeated northward incursions of the warmer waters from the proto-Gulf of Mexico, with their associated, distinctive, Tethyan faunal elements (Kauffman and Caldwell, 1993).

2.2.2 Bearpaw biostratigraphy

Throughout the Western Interior Basin, the Cretaceous marine sequences contain foraminiferal and molluscan faunas rich in number and variety. Both faunal groups have

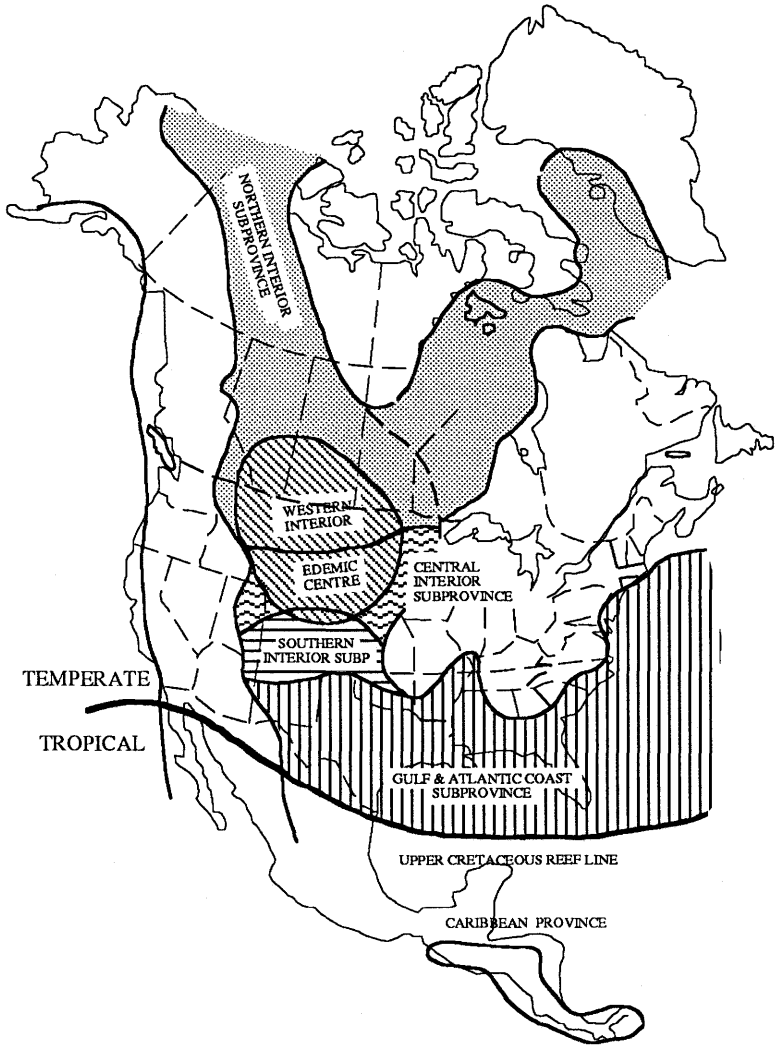


Fig 2.3 Map showing the average expression of Northern, Central and Southern Interior paleobiographic subprovinces from the Cretaceous Western Interior Seaway of North America. After Kauffman *et al.*(1993).

been used to develop biostratigraphic zonal schemes. The molluscan biostratigraphic system, applicable throughout the greater part of the basin, is among the most temporally refined in the world. The zonation has an average of 0.45-0.85 m.y./biozone for all Cretaceous stages (range 0.04-2.42 m.y./biozone), and 0.28-0.68 m.y./biozone for the Late Cretaceous stages (Kauffman *et al.*,1993), based on the new time-scale of Obradovich (1993). This precision has been achieved largely by the integration of well-studied evolutionary lineages of molluscs, in particular ammonites and various groups of bivalves. Fifty-nine ammonoid zones, based mostly on species of *Baculites,* have been identified for the Late Cretaceous sequences. The Bearpaw marine cyclothem spans up to eleven ammonite range zones, from the *Didymoceras nebrascense* Zone at the base to the *Baculites grandis* Zone at the top (Fig.2.4).

Both benthonic and pelagic foraminifera are present in the Cretaceous rocks of the basin, offering a viable alternative to the ammonites and inoceramid bivalves as a basis for biostratigraphic classification. However, compared to ammonites (the traditional zonal fossils), the foraminifera are intrinsically much less reliable biostratigraphic indicators for long-range correlation, because they were mainly benthonic, evolved more slowly, and few lineages have been identified (Caldwell *et al.*, 1993). At present, only about thirty successive foraminiferal faunas have been distinguished in the Cretaceous System of the basin (Caldwell *et al.*, 1978, 1993), six of which are found in the Bearpaw Formation of the study area (Fig. 2.4). From oldest to youngest, these are *Eoeponidella linki, Dorothia cf. smokyensis, Gaudryina bearpawensis, Praebulimina kickapooensis, Anomalinoides sp.,* and *Haplophragmoides excavata* (North and Caldwell, 1970, 1975; Caldwell *et al.*, 1978, 1993).

STAGES		AGES (m.y.)	AMMONITE ZONES	FORAMINIFERAL ZONES
MAASTRICHTIAN	lower	69.9	*B. grandis*	*HAPLOPHRAGMOIDES EXCAVATA*
		70.4	*B. baculus*	
		70.9	*B. eliasi*	
		71.4		
CAMPANIAN	upper	72.9	*B. jenseni*	*ANOMALINOIDES* SP.
		72.4	*B. reesidei*	
		72.9	*B. cuneatus*	*PRAEBULIMINA KICKAPOOENSIS*
		73.4	*B. compressus*	
		74.1	*D. cheyennense*	*GAUDRYINA BEARPAWENSIS*
		74.8	*E. jenneyi*	*DOROTHIA* SP.
		75.3	*D. stevensoni*	
		75.9	*D. nebrascense*	*EOEPONIDELLA LINKI*

Fig. 2.4 Biostratigraphy of the Bearpaw Formation and its equivalents of the Cretaceous Western Interior Basin of North America. For the ammonite genera, *B.* = *Baculites, D.* = *Didymoceras, E.* = *Exiteloceras.* Modified from Caldwell *et al.* (1978 , 1993) and Kauffman *et al.* (1993).

2.3 Sedimentary Environments

Most of the characteristics of the sediments and fossils suggest that the Bearpaw sea was shallow and that epineritic conditions prevailed (Gill and Cobban, 1966; Caldwell, 1968). Cross-bedding is found in the sands, and the clays are silty and massive, seldom showing any marked lamination, and some are bioturbated or contain trace fossils. Some bentonite seams have ragged contacts; others are no more than impersistent streaks, suggesting that the sedimentation of volcanic ash was possibly disrupted by bottom currents. The rich and varied molluscan fauna, together with linguloid and rhynchonelloid brachiopods and pyriporoid and membraniporoid bryozoans, could have thrived only at shallow depths (Caldwell, 1968).

The transgression and regression of the Bearpaw sea were not instantaneous, and thus the Bearpaw Formation and its equivalents are of different ages from place to place (Tourtelot, 1962; Caldwell 1968). The timing of transgression and regression also varied in different portions of the basin, indicating the effect of local crustal instability on transgression and regression of the seaway (Gill and Cobban, 1973). In the American portion of the basin, the Bearpaw shoreline moved farthest west in Montana during *Baculites compressus* time. However, in the southern Interior Plains of Canada, the western shoreline of the sea was restricted to southwestern Saskatchewan until *Baculites compressus* time when the sea swept rapidly across much of southern Alberta. It probably did not establish its most westerly shoreline until *Baculites cuneatus* or *Baculites reesidei* time, when the Snakebite Clay was accumulating in the South Saskatchewan River valley. The Bearpaw sea began to withdraw from Montana after *Baculites cuneatus* time, earlier than from the Canadian portion, where the sea receded

from Alberta into Saskatchewan between *Baculites eliasi* and *Baculites grandis* times (Caldwell, 1968, 1982; Kauffman and Caldwell, 1993). With the main transgression and regression, the environment of the southern Interior Plains of Canada in southern Alberta and southwestern Saskatchewan changed from near-shore to off-shore and back to near-shore, and smaller-scale changes repeated the main facies transitions in response to lower-order sea-level fluctuations.

Stratigraphic data show that while the Bearpaw sea invaded the southern Interior Plains of Canada and Montana, most of Wyoming remained emergent, and the western shore moved eastward in Colorado (Zapp and Cobban, 1962; Gill and Cobban, 1966, 1973; Caldwell, 1968; Cobban *et al.*, 1993). The large eastward bulge of the shorelines in northern Wyoming and southern Montana during the regressive phase outlines an elongate peninsula-like mass of dominantly nonmarine rocks, extending from northwestern Wyoming to eastern Montana and the western part of North and South Dakota. This mass is interpreted as a deltaic complex, the Sheridan delta (Gill and Cobban, 1973), which was an important paleogeographic feature of the basin during the Late Cretaceous Epoch. The Sheridan delta separated Montana, southeast Alberta, southwest Saskatchewan, and Wyoming into distinct depositional provinces. In the northern part of the Sheridan delta, the Mosby embayment existed, within which fine grained sediments of the Bearpaw Formation accumulated. In the east there was a more open environment, in which muds of the Pierre Shale were deposited.

3. PRESERVATION OF MOLLUSCAN FOSSILS

3.1 General Remarks

Stable isotopic and chemical compositions of the carbonate shells of fossils have been widely used in paleoenivronmental studies. The original isotopic ratios and chemical compositions of the shells, however, are not always preserved throughout geological time. Postformational processes, for example those associated with diagenesis, can result in the alteration of original carbonate minerals, such as the alteration of aragonite to calcite and of high-Mg calcite to low-Mg calcite (e.g., Reeder, 1983). During these processes, isotopic and chemical exchange reactions may occur. In addition to diagenetic processes, carbonate minerals may undergo simple isotope exchange with ambient fluids. Rates of diffusion, particularly solid-state diffusion, are infinitely small at low temperatures below 100^0C (O'Neil, 1987). Consequently, the only reasonable cause for isotope exchange is solution and redeposition, or recrystallization in the strict sense of breaking and reforming chemical bonds in the mineral. The chemical composition of the shell would also be affected during these processes.

It is widely accepted that alteration of the carbonate shell begins after the death of the organism. In usual circumstances, the tissues of the organism can decompose quickly, leaving the shell with no trace of soft parts. The shell is usually set upon by various other organisms, which drill or etch themselves into it or feed on it. Fungi, for example, may have used organic sheets and the siphuncular and mucus layers within the

chambers as a source of food (Dullo and Bandel, 1988). Both early decay of the organic shell material and boring by other organisms lead to marine cementation as liquids enter all open spaces of the shell. However, the stable isotopic and chemical compositions of the cement, formed before shells are buried, still represent those of the original seawater.

As soon as shells are buried, they may become affected by pore water, which may have isotopic and chemical compositions quite different from that of the original seawater. Under anaerobic conditions, pyrite crusts and phosphates commonly form, and aragonite begins to dissolve (Dullo and Bandel, 1988). During lithification, shells may be replaced by different materials, or they may totally disappear, leaving a mold which could later be filled isochemically or allochemically. Carbonate fossils may also pass through a phase of meteoric diagenesis. This diagenetic environment is characterized by freshwater of either a vadose or phreatic origin. High Mg-calcite and aragonite are unstable in freshwater and will be transformed into calcite. The predominant feature of the meteoric diagenetic environment is carbonate dissolution and redeposition.

Due to these processes, carbonate shells may be partially or completely altered, and consequently their stable isotopic and chemical compositions may no longer represent those of the original paleoenvironments in which the organisms lived but record those of the postformational fluids with which the shells came in contact. In order to obtain the most reliable data upon which to base original paleoenvironmental interpretations, therefore, well-preserved fossil shells must be identified. Physical and chemical methods were used in this research to investigate the state of preservation of molluscan fossils from the Bearpaw cyclothem, and in this way, criteria for recognizing

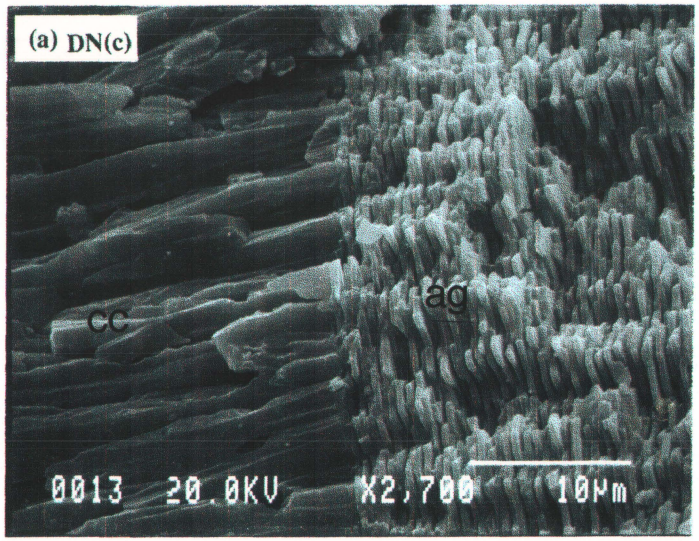
well-preserved fossils were determined.

3.2 Preservation of the Molluscan Fossils Collected

The molluscan fossils selected for the chemical and stable isotopic investigations were exclusively ammonites and inoceramids, which dominate the Bearpaw fauna. Ammonites used include baculitids, scaphitids, and a few specimens of *Didymoceras*, *Exiteloceras*, and *Menuites*. These fossils were collected from the holdings of the United States Geological Survey (USGS) in Denver, the Geological Survey of Canada (GSC) in Ottawa, and the Department of Geological Sciences at the University of Saskatchewan, and they span all the ammonite zones of the Bearpaw cyclothem (Fig. 2.4).

Molluscan shells are multilayered. The outermost organic layer, composed of chitin-like material, is called the periostracum; it is usually not preserved after diagenesis. Below the periostracum are two or more calcareous layers. The post-embryonic shell of ammonites consists of three principal carbonate layers (Birkelund, 1981); the outer prismatic layer made of calcite, the nacreous layer made of aragonite, and the inner prismatic layer made of calcite. Inoceramids have a shell of two calcareous layers; the inner nacreous layer made of aragonite and the outer prismatic layer made of calcite. The inner laminated nacreous layer has been preserved in most of the samples used in this study, especially the ammonites (Fig.3.1. a, b, and c) whose preservation is usually better than that of the bivalves. In some specimens, the nacreous layer is mildly altered (Fig.3.1. d and e), and in a few it is extensively or totally altered to calcite during later diagenesis (Fig. 3.1 f, g, and h). Diagenetic phosphate and especially pyrite were found

Fig. 3.1 SEM photomicrographs of the structure of ammonite shells in this study: **(a)** Completely preserved nacreous aragonite (ag) layer and prismatic calcite layer of *Baculites* (DN(c)); **(b)** Completely preserved nacreous aragonite layer of *Baculites scotti* (BS(e)); **(c)** Completely preserved aragonite layer of *Inoceramus* (DC(a)); **(d)** Mildly altered aragonite (ag) layer of *Baculites baculus* (BB(a)-1). Some parts of the shell were slightly altered into calcite (cc); **(e)** The outermost aragonite (ag) layer of *Baculites compressus robinsoni* (N70) has been transformed to blocky calcite (cc); **(f)** Aragonite (ag) layer of *Baculites compressus robinsoni* (N63) has partially altered to calcite (cc); **(g)** Extensively altered shell of *Baculites compressus* (N92). Most of the shell has been altered into blocky calcite (cc). Only a portion of aragonite (ag) is preserved; **(h)** The upper portion of aragonite (ag) layer of *Baculites compressus* (N90) has been transferred into calcite (cc). Secondary calcite formed the pseudoprismatic structure in some parts of the shell.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cc
ag
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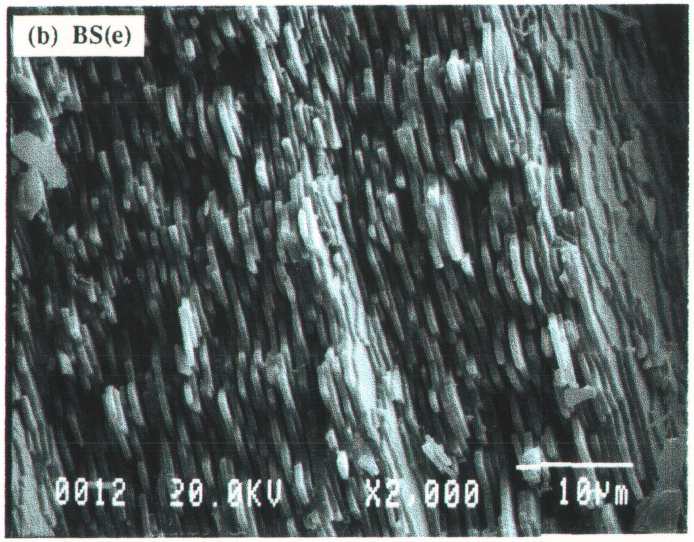
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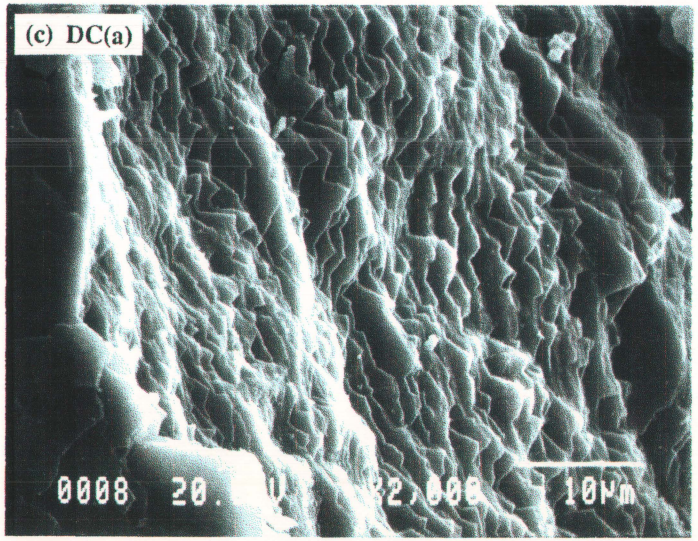
(c) DC(a)
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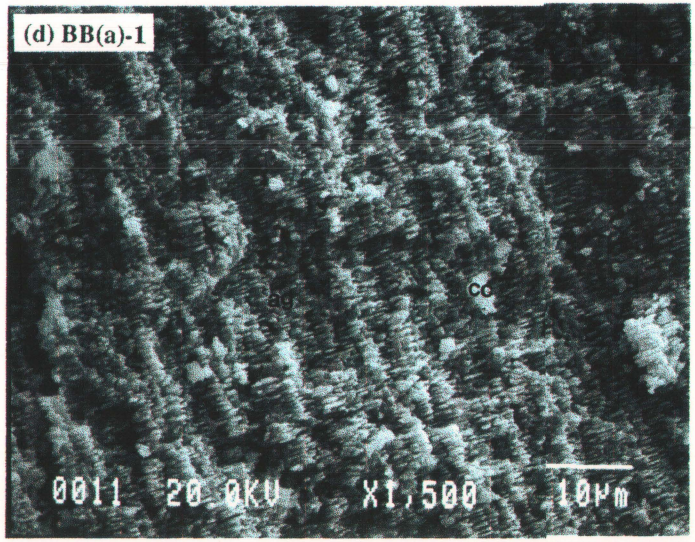
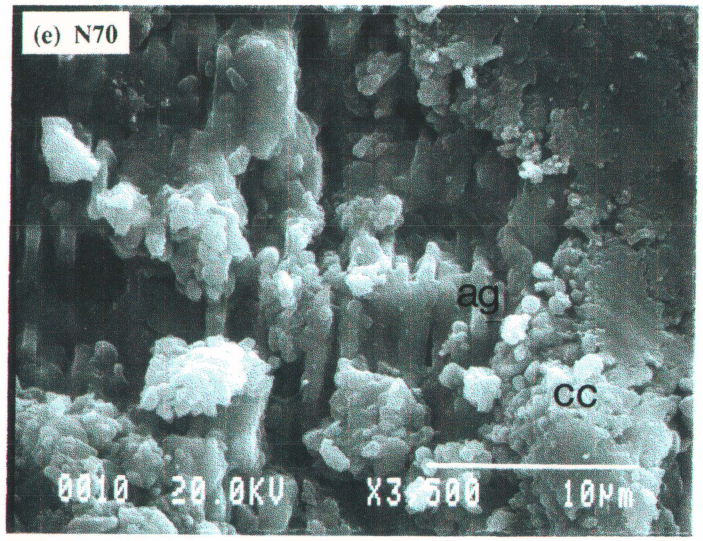
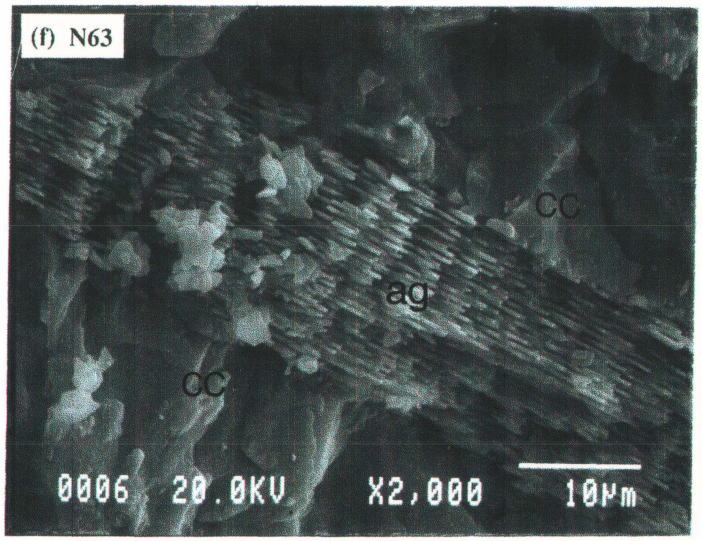

(d) BB(a)-1
ag
cc
0011 20.0KV X1,500 10μm


(e) N70
ag
cc
0010 20.0KV X3,500 10μm


(f) N63
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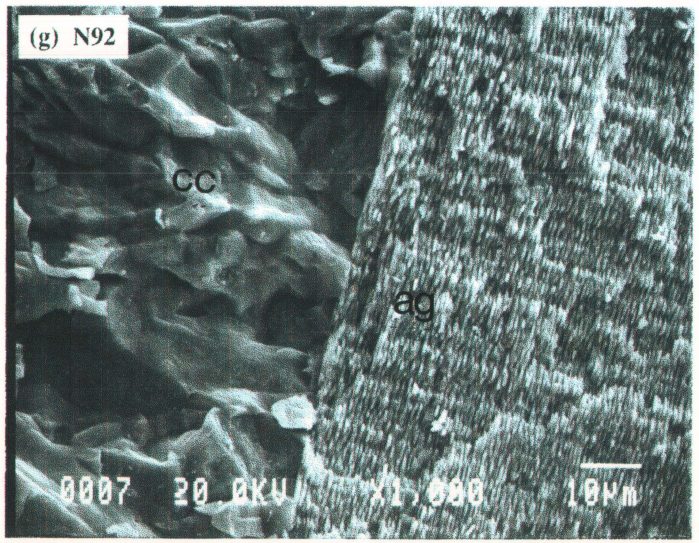
ag
cc
0006 20.0KV X2,000 10μm


(g) N92
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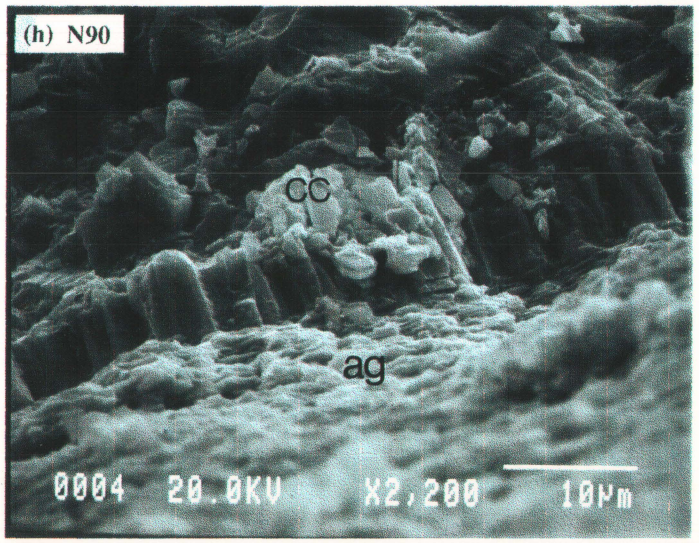
ag
0007 20.0KV X1,000 10μm


(h) N90
cc
ag
0004 20.0KV X2,200 10μm

in a few samples. These samples were avoided due to the potential effect on the chemical compositions of the shell carbonates.

The molluscan fossils of the Bearpaw Formation and equivalents occur mostly in concretions composed of fine-grained limestone (Caldwell, 1968; Gill and Cobban, 1966). Concretions are crucial for the preservation of aragonite layers in both ammonites and bivalves because these secondary sedimentary structures isolated the fossils from diagenetic and other postformational processes, and so protected the aragonite from oxidizing conditions that otherwise would have destroyed the organic matrix formed within it. This matrix is also important in preserving the carbonate minerals from postformational alteration. Decay of the matrix leads to differential accessibility by postformational fluids, which would partially (or totally) alter the original shells and thus change their chemical and isotopic compositions.

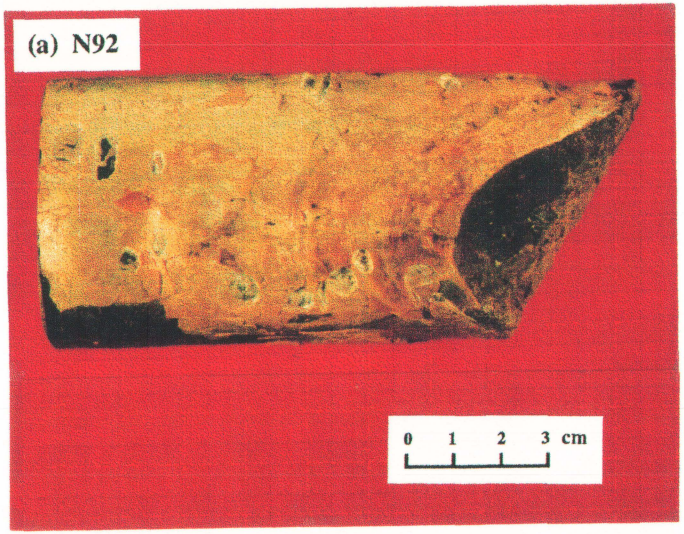
3.3 Criteria for Well-Preserved Fossils

Few fossils collected have preserved the prismatic calcite layer of their shells. As a result, only the aragonite layer was sampled for stable isotopic and chemical analyses. Another important reason for choosing aragonite is that it records alteration more readily than calcite, which can be easily distinguished from aragonite by x-ray diffraction (XRD) methods and then quantified. According to phase studies (Carlson, 1980; Reeder, 1983), only calcite, magnesite, and dolomite are expected to be stable under the Earth's surface conditions. Aragonite will gradually transform irreversibly into calcite near the Earth's surface. Therefore, aragonite from shells should be original and able to be used as a record of paleoenvironments.

Aragonite shells that have undergone extensive alteration can be easily recognized by visual examination. These shells are white and grey-white in color and are without pearly lustre (Fig.3.2 a, b) in contrast to well-preserved fossils whose shells are brown and grey-brown in color and show pearly lustre (Fig. 3.2 c). Some shells of extensively altered fossils can be lithified (Fig.3.2 b), or are soft and flake easily (Fig. 3.2 a). Mildly altered fossil shells, however, exhibit color ranging from pale brown (as in well-preserved shells) to more whitish or greyish-brown (Fig.3.2 d), and their degree of preservation cannot be determined visually. Consequently, detailed examination is required on the scale of scanning electron microscope (SEM) and x-ray diffraction (XRD) analysis. The question that arises then is: what is the maximum percent of secondary calcite that can be present in shells without negating their usefulness for stable isotopic and chemical analyses?

Before a large number of samples were analyzed, the relationship between stable isotopic compositions, chemical compositions and the amounts of secondary calcite in aragonitic shells was quantified. Thirty samples of shell aragonite, ranging from well-preserved ones with a content of calcite below the detection limit of XRD to very poorly preserved ones which are almost altered to calcite, were sampled for this purpose. After determining the contents of calcite using quantitative XRD methods (Davies and Hopper, 1963), the stable-isotope compositions of these samples were analyzed (Table 3.1). For samples with less than 5% secondary calcite, the $\delta^{18}O$ values are randomly distributed, and no correlation exists between the values and the contents of calcite (Fig.3.3 a). An excellent correlation exists, however, between the contents of secondary calcite and the $\delta^{18}O$ values of samples with more than 5% secondary calcite. In fact, the

Fig.3.2 Photographs of ammonite fossils with different degrees of preservation: **(a)** Extensively altered fossil of *Baculites compressus robinsoni* (N92). The shell is white or grey-white in color without pearly lustre. Alteration can be easily recognized by visual examination; **(b)** Shell of *Didymoceras nebrascense* (EJ(d)) is extensively altered, showing no pearly lustre. The shell carbonate is lithified during diagenesis; **(c)** Well-preserved fossil of *Baculites* (DN(c)). Its shell is brown and grey-brown in color without any detectable traces of secondary calcite and shows pearly lustre; **(d)** Mildly altered fossil of *Baculites scotti* (BS(d)). The shell is more grey in color than well-preserved shells, showing some degree of pearly lustre. Secondary calcite can be recognized by SEM and XRD methods.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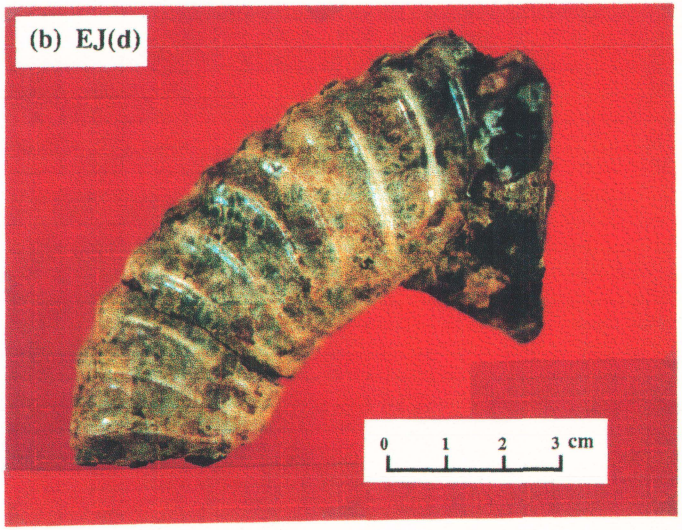
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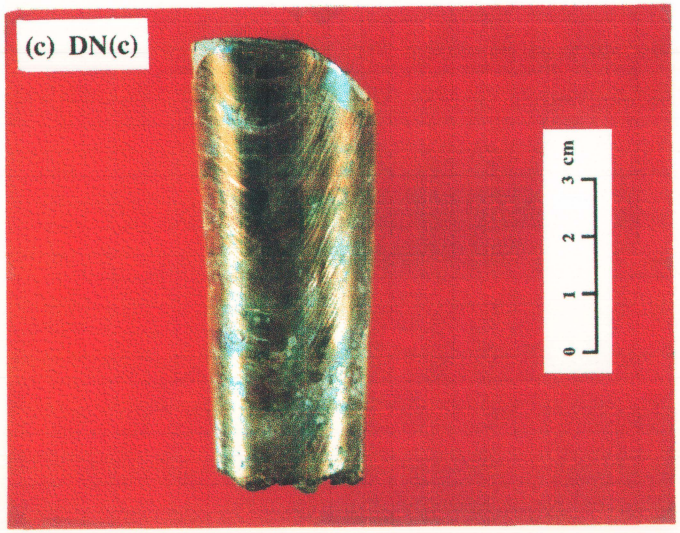
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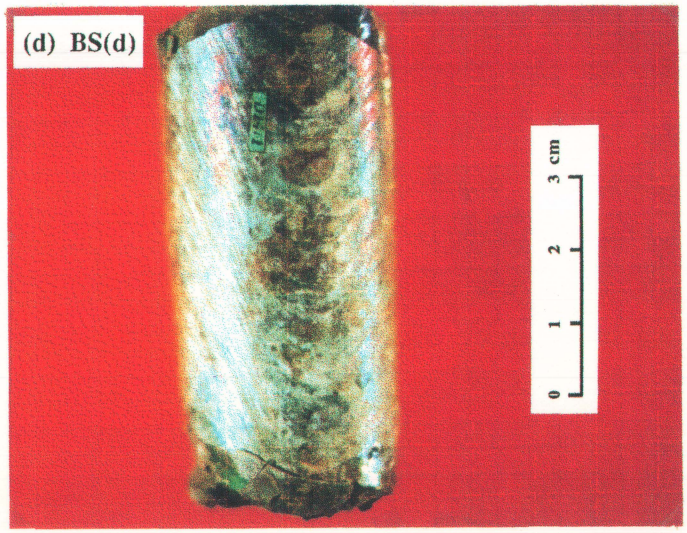

(d) BS(d)
0 1 2 3 cm

Table 3.1 $\delta^{18}O$ and $\delta^{13}C$ values in aragonite of baculitid shells with different contents of secondary calcite

Sample	Taxon	$\delta^{13}C$	$\delta^{18}O$	Secondary calcite
N94(6)	*B. compressus robinsoni*	-1.27	-1.36	7.8
N92(1)	*B. compressus robinsoni*	-1.24	-2.15	11.0
N92(2)	*B. compressus robinsoni*	-1.20	-3.06	21.5
N92(3)	*B. compressus robinsoni*	-2.59	-1.80	11.3
N92(4)	*B. compressus robinsoni*	2.70	-4.87	40.0
N39(3)	*B. compressus robinsoni*	0.17	-2.60	12.0
N92(5)	*B. compressus robinsoni*	-2.80	-1.78	4.5
N92(7)	*B. compressus robinsoni*	-2.78	-1.73	4.0
N92(8)	*B. compressus robinsoni*	1.34	-4.24	60.0
N92(9)	*B. compressus robinsoni*	0.47	-3.62	49.0
N92(10)	*B. compressus robinsoni*	-0.24	-2.89	27.5
N92(11)	*B. compressus robinsoni*	0.75	-3.23	38.0
N92(12)	*B. compressus robinsoni*	-2.00	-1.97	8.5
N92(13)	*B. compressus robinsoni*	-2.62	-1.79	4.0
N92(14)	*B. compressus robinsoni*	-2.87	-1.78	3.8
N92(15)	*B. compressus robinsoni*	-2.37	-1.73	3.5
N92(16)	*B. compressus robinsoni*	-2.82	-2.18	9.0
N70(1)	*B. compressus robinsoni*	-2.21	-0.98	2.0
N70(2)	*B. compressus robinsoni*	-2.50	-0.73	1.5
N70(3)	*B. compressus robinsoni*	-4.79	-1.72	2.0
N70(4)	*B. compressus robinsoni*	-0.87	-1.50	7.0
N94	*B. compressus robinsoni*	-1.47	-1.75	6.5
N94(6)	*B. compressus robinsoni*	-1.27	-1.36	7.8
BR(c)-1	*B. reesidei*	-1.26	-2.05	0.3
Br(c)-2	*B. reesidei*	-1.11	-2.06	2.0
Br(c)-3	*B. reesidei*	-1.10	-1.54	3.5
N69(1)	*B. reesidei*	-1.30	-1.22	2.0
N69(2)	*B. reesidei*	-1.90	-1.23	2.5
N69(3)	*B. reesidei*	-3.10	-1.27	4.0
N63	*B. baculus*	-3.10	-2.63	3.5
LSD	*B. baculus*	-1.87	-0.84	4.0

Note: *B.* = *Baculites*. Isotopic values in per mil and calcite contents in percent. Most of the specimens are from the South Saskatchewan River valley. A series of numbers related to one individual specimen indicates different samples from that specimen. The specimen BR(c) is from Wyoming in the United States. The accuracy of X-ray diffraction analysis and precision of stable-isotope analysis are discussed in the APPENDIX I.

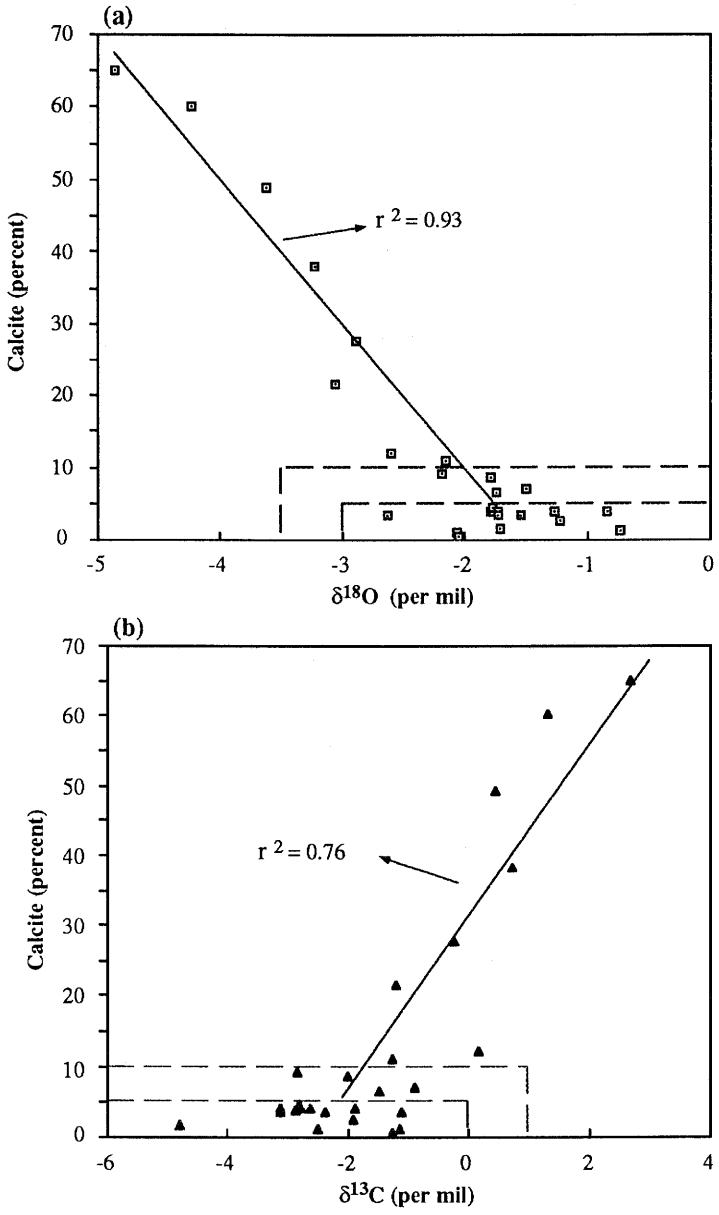


Fig 3.3 Distribution of the $\delta^{18}O$ **(a)** and $\delta^{13}C$ **(b)** values and secondary calcite contents in aragonite within shells of baculitids. The data are from Table 3.1. Solid lines in **(a)** (Cc = -30.16 - 19.98 x $\delta^{18}O$) and **(b)** (Cc = 30.76 + 12.27 x $\delta^{13}C$) through data of samples with more than 5% calcite. Cc represents the calcite contents.

results show that an amount of secondary calcite up to 10% would not significantly affect the oxygen-isotope compositions, considering that their isotope values are still within the range of those of well-preserved samples. In contrast to oxygen-isotope compositions, the carbon-isotope compositions of the aragonite of the shells are less sensitive to alteration. For samples with more than 5% secondary calcite, the correlation between the $\delta^{13}C$ values and the amount of calcite is poorer than that between the $\delta^{18}O$ values and the amount of calcite (Fig.3.3 b). This may reflect the fact that the difference between the carbon-isotope compositions of the shells and of the postformational fluids is less than that for the oxygen-isotope compositions. Postformational fluids, such as meteoric water, generally have much more negative oxygen-isotope values than those of original seawater. For example, modern meteoric water in Manitoba has a $\delta^{18}O$ value of -14 to -19 per mil, and that in Montana of -13 to -18 per mil (Cadrin *et al.*, 1996). Consequently, the oxygen-isotope composition of shell carbonate is more readily affected by postformational fluids. To err on the side of caution, only samples with less than 5 % secondary calcite were selected for stable-isotope analysis.

Relative to stable-isotope compositions, chemical compositions of fossil shells are more affected by secondary calcite (Buchardt and Weiner, 1981; Whittaker, 1989). Figure 3.4 shows the relationship between the secondary calcite contents and chemical compositions of fossil samples with different degrees of preservation. For samples with less than 3% secondary calcite, Mg/Ca ratios are distributed randomly, but in the range of modern molluscan shells, indicating that no corrections exist between the Mg/Ca ratios and calcite contents, and that the samples are not greatly affected by alteration. Samples with more than 3% secondary calcite have higher magnesium concentrations,

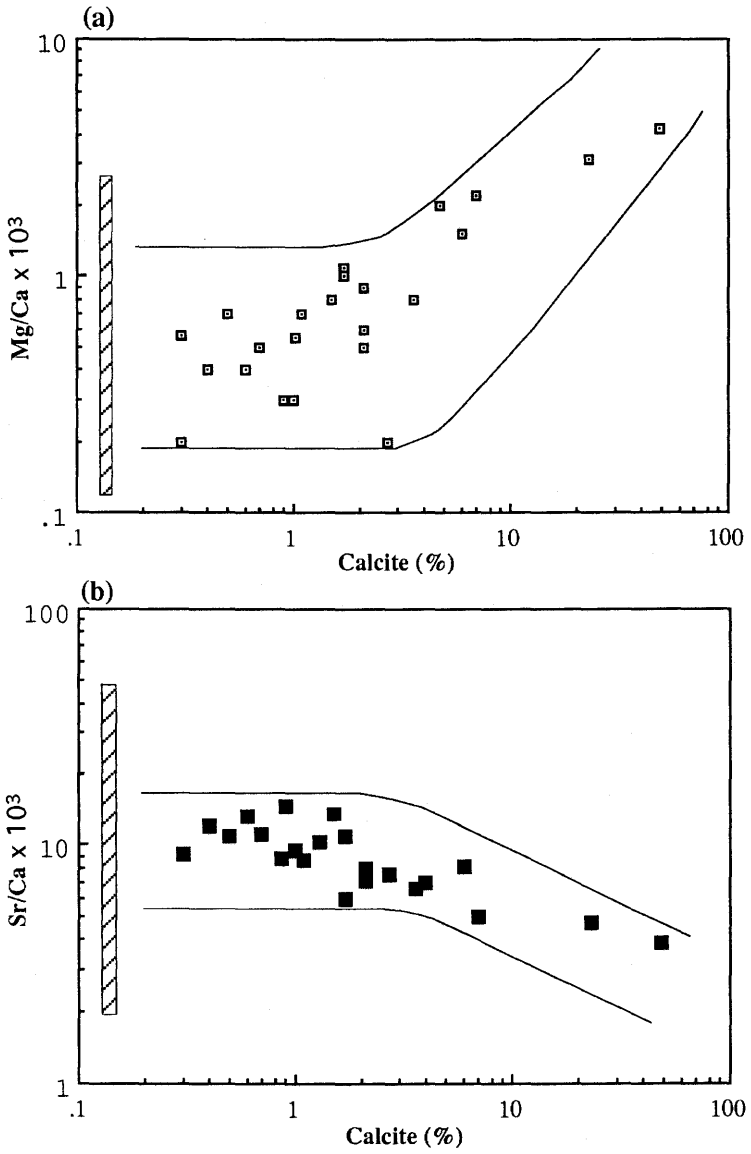


Fig. 3.4 Relation between Mg/Ca(a) and Sr/Ca (b) ratios, and calcite contents in aragonite of molluscan shells with different degrees of preservation. The shadow areas in (a) and(b) show the ranges of Mg/Ca and Sr/Ca ratios respectively within aragonite of modern molluscan shells (Buchardt and Weiner, 1981). Some data are from Whittaker (1989).

and Mg/Ca ratios increase with the increase of calcite contents to extend gradually beyond the range of modern molluscan shells. The strong correlation between calcite contents and Mg/Ca ratios is an expression of progressive diagenetic modification, leading towards total replacement of the aragonite of the shells by secondary calcite. The sensitivity of the Mg/Ca ratios of the shells to modification is attributed to the distinct chemical characteristics of the original seawater and secondary fluids responsible for alteration (Buchardt and Weiner, 1981). Calcite crystals formed in equilibrium with pore-water of a composition close to that of seawater will have magnesium concentrations 10 to 100 times greater than those of aragonite precipitated by marine molluscs (e.g., Bathurst, 1975). Therefore, even small amounts of early diagenetic calcite may be inferred from the magnesium data. Sr/Ca ratios are not affected by secondary alteration as significantly as Mg/Ca ratios, but they decrease slightly with an increase of secondary calcite contents in samples with more than 3% calcite. In summary, for the purpose of chemical analysis, only aragonite shells containing less than 3% secondary calcite can be considered well-preserved samples to be used for trace-element analysis.

Unlike aragonite, it is much more difficult to discern secondary calcite from the original calcite of fossils shells. Understanding the mineralogy and microstructure of modern representatives of the organisms is essential to selecting original calcite shells for chemical investigation. Different species of organisms consist of different carbonate minerals (Milliman *et al.*, 1974). Most organisms have a skeleton of either aragonite or high-Mg calcite; only a few are composed of low-Mg calcite. If a specific shell does not have the inferred primary mineral composition, it may have been altered. In most cases,

microstructures of the shells will change with transformation of skeletons from high-Mg to low-Mg calcite or recrystallization of low-Mg calcite. For foraminifera, their original microstructure should be composed of tiny particles of micrite (dark, or extremely fibrous), but after alteration, the most common structure is a crystalline structure, which may be coarse.

Cathodoluminescence (CL) examination can be an important adjunct to conventional petrographic and SEM observations. Luminescence in carbonates is most commonly activated by a Mn^{2+} concentration of approximately 100 ppm (Machel, 1985). Carbonate shells of modern organisms usually contain low Mn concentrations and do not luminesce (Popp *et al.*, 1986). Chemical and isotopic parameters can also be used to discern altered calcitic shells because diagenesis usually results in variations in stable-isotope values and trace-element concentrations. However, although the above methods can be used, it is still difficult to quantify the alteration of the calcitic shells due to the problem of calculating the amount of secondary calcite present. Therefore, shell aragonite, if available, is the ideal material for stable isotopic and chemical investigations of paleoenvironments.

4. STABLE ISOTOPIC GEOCHEMISTRY OF MOLLUSCAN FOSSILS

4.1 Introduction

Urey first theorized in 1947 that stable isotopes could be used to decipher paleoenvironmental conditions. The basic principles of this theory are simple and straightforward: the stable-isotope composition of a mineral deposited in stable-isotope equilibrium with ambient water depends strictly on the temperature, salinity, and isotopic composition of the water. The stable-isotope compositions of carbonate fossils can, therefore, provide insights into the temperature, salinity, and stable-isotope composition of the water in which the organisms lived. As stable isotopes of carbonate shells may record the paleoenvironmental conditions during the entire life-time of an organism, information on the mode of life of extinct organisms, such as ammonites, can be deduced through study of stable-isotope compositions of their shells. The ontogenetic history of organisms can also be inferred by investigating stable-isotope compositions of successive growth increments of their shells.

The Western Interior Seaway is unique and fundamentally different from most Cenozoic and modern marginal, epicontinental, and epeiric seas because both circum-polar and subtropical oceans contributed to its formation (Kauffman and Caldwell, 1993). In addition to these two water masses, low-salinity surface water has always been suggested as a third possible aqueous component of the seaway, primarily as a

result of relatively low $\delta^{18}O$ values of molluscan fossils found in the basin (Kauffman, 1975; Wright, 1987; Kyser *et al.* 1993). Understanding the nature of the seawater will provide a clue to the meeting and mixing of these watermasses in the seaway. The purpose of this section is to investigate the stable-isotope compositions of molluscan fossils from the Bearpaw cyclothem in combination with other geological data, to study the character of the water within the seaway, and to deduce its paleoenvironment from Late Campanian to Early Maastrichtian times. The mode of life and ontogenetic history of ammonites that lived within the seaway are also analyzed by comparing their stable-isotope compositions with those of other coexisting molluscan fossils.

4.2 Results

Aragonite shells of molluscan fossils from the Bearpaw cyclothem, collected from the central portion of the basin, were sampled and examined by SEM and XRD to check for secondary alteration. Well-preserved samples, which fit the criteria discussed in the previous section, were chosen for stable isotopic analysis (Table 4.1).

There is marked heterogeneity in the stable-isotope compositions of coexisting molluscan fossils throughout the central portion of the basin (Fig.4.1 and Table 4.1). Generally, inoceramid shells have the highest $\delta^{13}C$ values (0.6 to 5.0 ‰) and the lowest $\delta^{18}O$ values (-4.7 to -2.8 ‰), whereas baculitid shells have the highest $\delta^{18}O$ values (0.0 to -2.8‰) and the lowest $\delta^{13}C$ values (-4.8 to -0.3 ‰). The isotopic compositions of other molluscan shells are generally between the ranges of baculitids and inoceramids, with *Didymoceras* and *Exiteloceras* having lower $\delta^{18}O$ values (-1.9 to -2.3 ‰) and higher $\delta^{13}C$ values (1.0 to 1.8 ‰) than baculitids, and *Menuites* having the same range of

Table 4.1 Sample descriptions of molluscan fossils from the Bearpaw cyclothem and their stable-isotope compositions

Sample	Ammonite Zone	Taxon	Sample Locality	$\delta^{13}C$	$\delta^{18}O$
LSD 12	*B. baculus*	*B. baculus*	Frenchman River valley, Sask.	-1.45	-0.97
LSD 12a	*B. baculus*	*B. baculus*	Frenchman River valley, Sask.	-1.87	-0.84
LSD	*B. baculus*	*B. baculus*	Frenchman River valley, Sask.	-1.14	0.06
N27	*B. cuneatus*	*B. cuneatus*	Cypress Hills, Sask.	-1.10	-2.03
N25	*B. cuneatus*	*B. cuneatus*	Cypress Hills, Sask.	-0.72	-0.53
N28	*B. cuneatus*	*B. cuneatus*	Cypress Hills, Sask.	-1.70	-0.44
N29	*B. cuneatus*	*B. cuneatus*	Cypress Hills, Sask.	-1.47	-2.20
N69(1)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-1.34	-1.22
N69(2)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-1.87	-1.23
N69(3)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-3.10	-1.27
N61(a)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-1.82	-1.01
N61(b)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-1.21	-1.35
N47a	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-2.11	-1.15
N73a(1)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-2.25	-1.47
N73a(2)	*B. reesidei*	*B. reesidei*	South Sask. River valley, Sask.	-1.34	-1.31
N94	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-1.28	-1.36
N92(1)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.00	-1.97
N92(2)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.62	-1.79
N92(3)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.87	-1.78
N92(4)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.37	-1.73
N92(5)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.80	-1.78
N77	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.11	-2.21
N70(1)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.21	-0.98
N70(2)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.50	-0.73
N70(3)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.79	-1.72
N70(4)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-1.78	-1.31
N71(1)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-0.49	-1.35
N71(2)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-0.66	-1.42
N71(3)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-1.33	-1.63
N71(4)	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-0.87	-1.50
N65	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-3.52	-1.37
N81	*B. compressus*	*B. compressus robinsoni*	South Sask. River valley, Sask.	-2.04	-1.15
SBS(a)	*B. scotti*	*B. scotti*	Millwood, Manitoba	-0.90	0.02
SBS(b)	*B. scotti*	*B. scotti*	Millwood, Manitoba	-0.66	0.26
SBS(c)	*B. scotti*	*B. scotti*	Millwood, Manitoba	-1.40	0.40
SBS(d)	*B. scotti*	*B. scotti*	Millwood, Manitoba	-0.69	0.52
N95(1)	*B. eliasi*	*S. plenus*	South Sask. River valley, Sask.	1.94	-1.51
N95(2)	*B. eliasi*	*S. plenus*	South Sask. River valley, Sask.	1.98	-1.65
N95(3)	*B. eliasi*	*S. plenus*	South Sask. River valley, Sask.	1.30	-1.52
OT	*E. jenneyi*	*Inoceramus sp.*	South Sask. River valley, Sask.	0.55	-3.79
BS(a)	*B. scotti*	*Eutrephoceras sp.*	Fall River, South Dakota	-0.37	-0.23
BS(b)	*B. scotti*	*Menuites*	Fall River, South Dakota	-0.34	0.42
BS(e)-1	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.25	-0.48
BS(e)-2	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.30	0.01
BS(e)-3	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.45	-0.25
BS(e)-1SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.43	-0.19
BS(e)-2SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.62	-0.46
BS(e)-3SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.66	-0.25
BS(e)-4SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-1.47	-0.68
BS(e)-5SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-0.87	-0.59
BS(e)-6SF	*B. scotti*	*B. scotti*	Fall River, South Dakota	-0.78	-0.75
BS(f)-1	*B. scotti*	*I. sublaevis*	Fall River, South Dakota	3.59	-3.00
BS(f)-2	*B. scotti*	*I. sublaevis*	Fall River, South Dakota	3.27	-3.16
BS(f)-3	*B. scotti*	*I. sublaev0is*	Fall River, South Dakota	4.03	-3.09
BS(g)-1	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-3.18	-1.80
BS(g)-2	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-2.61	-1.54
BS(g)-3	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-2.65	-1.19
BS(g)-4	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-3.01	-1.36
BS(g)-5	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-3.37	-0.62
BS(g)-6	*B. scotti*	*Menuites sp.*	Fall River, South Dakota	-4.63	-0.77
DN(1)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.45	-1.92
DN(2)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	0.96	-2.06

Table 4.1 (continued 1)

Sample	Ammonite Zone	Taxon	Sample Locality	$\delta^{13}C$	$\delta^{18}O$
DN(3)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	0.87	-2.25
DN(4)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.09	-2.14
DN(5)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.32	-2.13
DN(6)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.77	-2.00
DN(7)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.57	-2.29
DN(8)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.82	-2.00
DN(9)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.18	-2.09
DN(10)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.62	-1.94
DN(11)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.39	-2.16
DN(12)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.43	-2.02
DN	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.57	-1.91
DN(1)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.21	-2.13
DN(2)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.39	-2.20
DN(3)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.18	-2.41
DN(5)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.21	-2.13
DN(6)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.80	-2.13
DN(7)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.79	-2.03
DN(8)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.94	-1.99
DN(9)SF	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.52	-2.34
DN(a)	*D.nebrascense*	*D.nebrascense*	Fall River, South Dakota	1.61	-1.85
DN(b)-1	*D.nebrascense*	*Baculites sp.*	Fall River, South Dakota	-2.57	-0.32
DN(b)-2	*D.nebrascense*	*Baculites sp.*	Fall River, South Dakota	-2.20	-0.43
DN(c)	*D.nebrascense*	*Baculites sp.*	Fall River, South Dakota	-1.96	-0.26
DN(c)-1	*D.nebrascense*	*Baculites sp.*	Fall River, South Dakota	-2.06	-0.73
DN(c)-7	*D.nebrascense*	*Baculites sp.*	Fall River, South Dakota	-1.66	-0.05
DS(b)	*D. stevensoni*	*Inoceramus sp.*	Albany, Wyoming	3.90	-3.75
DS(c)-a	*D. stevensoni*	*Baculites sp.*	Albany, Wyoming	-0.56	-2.32
DS(c)-b	*D. stevensoni*	*Baculites sp.*	Albany, Wyoming	-0.14	-2.85
DS(c)-c	*D. stevensoni*	*Baculites sp.*	Albany, Wyoming	-0.83	-2.62
EJ(a)-1	*E. jenneyi*	*Inoceramus sp.*	Carter, Montana	1.86	-2.62
EJ(a)-2	*E. jenneyi*	*Inoceramus sp.*	Carter, Montana	3.78	-4.68
EJ(b)-1	*E. jenneyi*	*scaphite*	Carter, Montana	-0.53	-1.00
EJ (b)-2	*E. jenneyi*	*scaphite*	Carter, Montana	-1.24	-1.28
EJ(d)	*E. jenneyi*	*E. jenneyi*	Carter, Montana	0.88	-3.34
DC(a)-1	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.73	-3.59
DC(a)-2	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.87	-3.68
DC(a)-3	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.77	-3.72
DC(a)-4	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	5.02	-3.55
DC(a)-5	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.99	-3.50
DC(a)-6	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.79	-3.49
DC(a)-7	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.97	-3.43
DC(a)-8	*D. cheyennense*	*Inoceramus sp.*	Pennington, South Dakota	4.96	-3.45
DC(b)-1	*D. cheyennense*	*D. cheyennense*	Pennington, South Dakota	1.90	-1.55
DC(b)-2	*D. cheyennense*	*D. cheyennense*	Pennington, South Dakota	1.40	-1.77
DC(b)-3	*D. cheyennense*	*D. cheyennense*	Pennington, South Dakota	2.24	-1.62
DC(b)-4	*D. cheyennense*	*D. cheyennense*	Pennington, South Dakota	1.55	-1.88
DC(e)-a	*D. cheyennense*	*Baculites sp.*	Pennington, South Dakota	-0.60	-0.08
DC(e)-b	*D. cheyennense*	*Baculitee sp.*	Pennington, South Dakota	-1.09	-0.33
BC(a)	*B. compressus*	*B. compressus*	Pennington, South Dakota	-3.88	-2.05
BC(b)-1	*B. compressus*	*B. compressus*	Pennington, South Dakota	-2.97	-1.27
BC(b)-2	*B. compressus*	*B. compressus*	Pennington, South Dakota	-0.47	-1.66
BC(b)-3	*B. compressus*	*B. compressus*	Pennington, South Dakota	-2.54	-1.80
BC(b)-4	*B. compressus*	*B. compressus*	Pennington, South Dakota	-2.47	-1.97
BC(c)	*B. compressus*	*Acanthoscaphites sp.*	Pennington, South Dakota	-2.92	-3.05
BC(d)	*B. compressus*	*Baculites sp.*	Pennington, South Dakota	-1.63	-1.71
BCN(a)-1	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.31	-0.94
BCN(a)-2	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.35	-0.70
BCN(a)-3	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.69	-1.18
BCN(a)-4	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.40	-0.72
BCN(a)-5	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.72	-1.02
BCN(a)-6	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.97	-1.42
BCN(a)-7	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-3.47	-1.21
BCN(a)-8	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-3.21	-1.65
BCN(a)-9	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.81	-1.66

Table 4.1 (continued 2)

Sample	Ammonite Zone	Taxon	Sample Locality	$\delta^{13}C$	$\delta^{18}O$
BCN(a)-10	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.21	-1.41
BCN(a)-11	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-1.77	-1.63
BCN(a)-7SF	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-2.25	-0.47
BCN(a)-8SF	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-3.40	-0.84
BCN(a)-11SF	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-1.94	-1.56
BCN(a)-12SF	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-1.23	-1.83
BCN(b)-a	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	0.15	-0.85
BCN(b)-b	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-0.03	-0.89
BCN(b)-c	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	0.59	-0.99
BCN(d)	*B. cuneatus*	*B. cuneatus*	Haakon, South Dakota	-1.24	-1.11
BCN(e)-1	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.41	-0.91
BCN(e)-2	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.46	-0.91
BCN(e)-3	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.35	-0.86
BCN(e)-4	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.48	-0.93
BCN(e)-5	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.03	-1.01
BCN(e)-6	*B. cuneatus*	*B. cuneatus*	SouthDakota	-4.41	-1.18
BCN(c)	*B. cuneatus*	*Inoceramus*	SouthDakota	4.52	-2.82
BR(c)-1	*B. reesidei*	*B. reesidei*	Wyoming	-1.26	-2.05
BR(c)-2	*B. reesidei*	*B. reesidei*	Wyoming	-1.11	-2.06
BR(c)-3	*B. reesidei*	*B. reesidei*	Wyoming	-1.10	-1.54
BR(c)-4	*B. reesidei*	*B. reesidei*	Wyoming	-1.02	-1.73
BJ(a)-1	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.67	-0.86
BJ(a)-2	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.59	-0.85
BJ(a)-3	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.46	-0.89
BJ(a)-4	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.27	-1.08
BJ(a)-5	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.49	-1.38
BJ(b)-1	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.73	-0.49
BJ(b)-2	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.53	-0.41
BJ(b)-3	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.56	-0.50
BJ(b)-4	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.53	-0.26
BJ(b)-5	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.51	-0.57
BJ(b)-6	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.62	-0.57
BJ(b)-7	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.40	-0.67
BJ(b)-8	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-0.30	-0.48
BJ(b)-9	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-1.00	-0.77
BJ(b)-10	*B. jenseni*	*B. jenseni*	Huerfano, Colorado	-1.47	-1.38
BE(c)	*B. eliasi*	*B. eliasi*	Crook, Wyoming	-3.39	-0.60
BE(d)-a	*B. eliasi*	*B. eliasi*	Crook, Wyoming	-4.07	-0.16
BE(d)-b	*B. eliasi*	*B. eliasi*	Crook, Wyoming	-3.89	-0.48
BB(d)	*B. baculus*	*B. baculus*	Haakon, South Dakota	-1.96	-0.07
BB(a)	*B. baculus*	*B. baculus*	Niobrara, Wyoming	-0.47	-2.63
BG-a	*B. grandis*	*B. grandis*	Pennington, South Dakota	-1.27	-0.60
BG-b	*B. grandis*	*B. grandis*	Pennington, South Dakota	-1.97	-0.63
BG-c	*B. grandis*	*B. grandis*	Pennington, South Dakota	-1.63	-0.33
BG-d	*B. grandis*	*B. grandis*	Pennington, South Dakota	-1.59	-0.21
BL(a)-1	*B. clinolobatus*	*Discoscaphites constrictus*	Dewey, South Dakota	-1.43	0.13
BL(a)-2	*B. clinolobatus*	*Discoscaphites constrictus*	Dewey, South Dakota	-2.06	0.14
BL(a)-3	*B. clinolobatus*	*Discoscaphites constrictus*	Dewey, South Dakota	-1.92	0.20
BL(a)-4	*B. clinolobatus*	*Discoscaphites constrictus*	Dewey, South Dakota	-1.02	-0.05
BL(b)-a	*B. clinolobatus*	*B. clinolobatus*	Dewey, South Dakota	-1.02	-0.05
BL(b)-b	*B. clinolobatus*	*B. clinolobatus*	Dewey, South Dakota	-0.62	0.22
BL(d)-a	*B. clinolobatus*	*Pholadomya sp.*	Carson, South Dakota	0.36	0.08
BL(d)-b	*B. clinolobatus*	*Pholadomya sp.*	Carson, South Dakota	0.31	0.19
BL(e)-a	*B. clinolobatus*	*B. clinolobatus*	Carson, South Dakota	-1.17	-0.37
BL(e)-b	*B. clinolobatus*	*B. clinolobatus*	Carson, South Dakota	-1.85	-0.37
BL(f)-a	*B. clinolobatus*	*B. clinolobatus*	Haakon, SouthDakota	-1.74	-0.54

Note: Fossil samples from the same ammonite zone in the United States have the same letter at the begining of the sample number. Samples from Canada keep the origional sample numbers as collected. Letters in brackets refer to different specimens from the same zone. A series of numbers related to one individual indicates samples taken along the length of the specimen. Letters following a dash refer to different samples from the same specimen. Abbreviations: *B. = Baculites, D. = Didymoceras, E. = Exiteloceras, S. = Scaphite, I = Inoceramus,* Sask. = Saskatchewan. The precision of stable isotopic analysis is discussed in APPENDIX I.

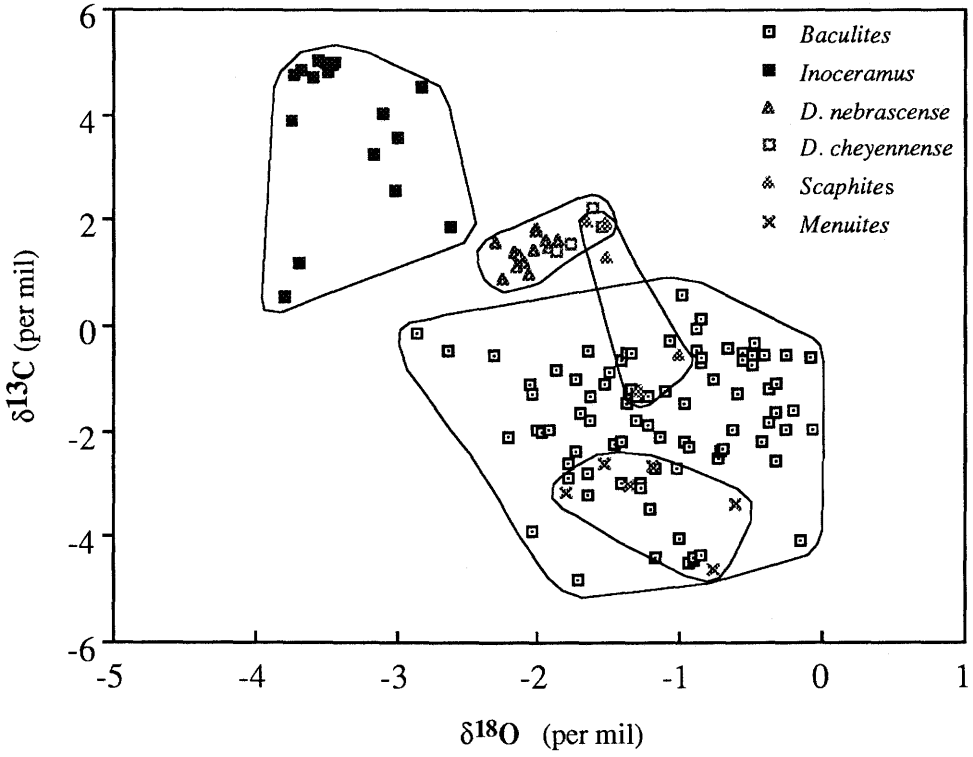


Fig. 4. 1 Relation between $\delta^{13}C$ and $\delta^{18}O$ values in aragonite of molluscan shells from the sedimentary rocks of the Bearpaw cyclothem in the central portion of the Western Interior Basin of North America. *D.* = *Didymoceras*. The data are from Table 4.1.

stable-isotope compositions as baculitids. Some scaphitids have stable-isotope compositions similar to those of *Didymoceras*, whereas others fall within the range of the baculitids.

Although the exact stratigraphic positions of all the fossils within the biostratigraphic zonal framework are unknown, the $\delta^{18}O$ values of the baculitids from places in the central portion of the basin vary with biostratigraphic sequence (Fig 4.2). For example, the baculitids from the *B. compressus, B. cuneatus,* and *B. reesidei* zones, denoting the period of most widespread transgression, have the lowest average $\delta^{18}O$ values (-2.3 to -0.7‰), whereas those from the underlying and overlying zones have higher $\delta^{18}O$ values (-1.38 to +0.01‰). The $\delta^{13}C$ values also change with the zonal sequence, but not necessarily in relation to the $\delta^{18}O$ values. Generally, the baculitids with higher $\delta^{18}O$ values have lower $\delta^{13}C$ values. Differences also exist in the stable-isotope compositions of different specimens of baculitids from the same ammonite zone, and such differences can be ca.1.0 ‰ for the $\delta^{18}O$ values and ca. 2.0 ‰ for the $\delta^{13}C$ values (Fig. 4.2).

Multiple analyses of molluscan shells indicate that variations in stable-isotope compositions occur within a single shell along the direction of growth (Fig. 4.3). Although the majority of molluscan shells have small variations of about 0.5 ‰ in both oxygen- and carbon-isotope compositions, some ammonites have relatively larger variations of 1.5 ‰ in $\delta^{18}O$ values and more than 2.0 ‰ in $\delta^{13}C$ values (Table 4.1 and Fig. 4.3).

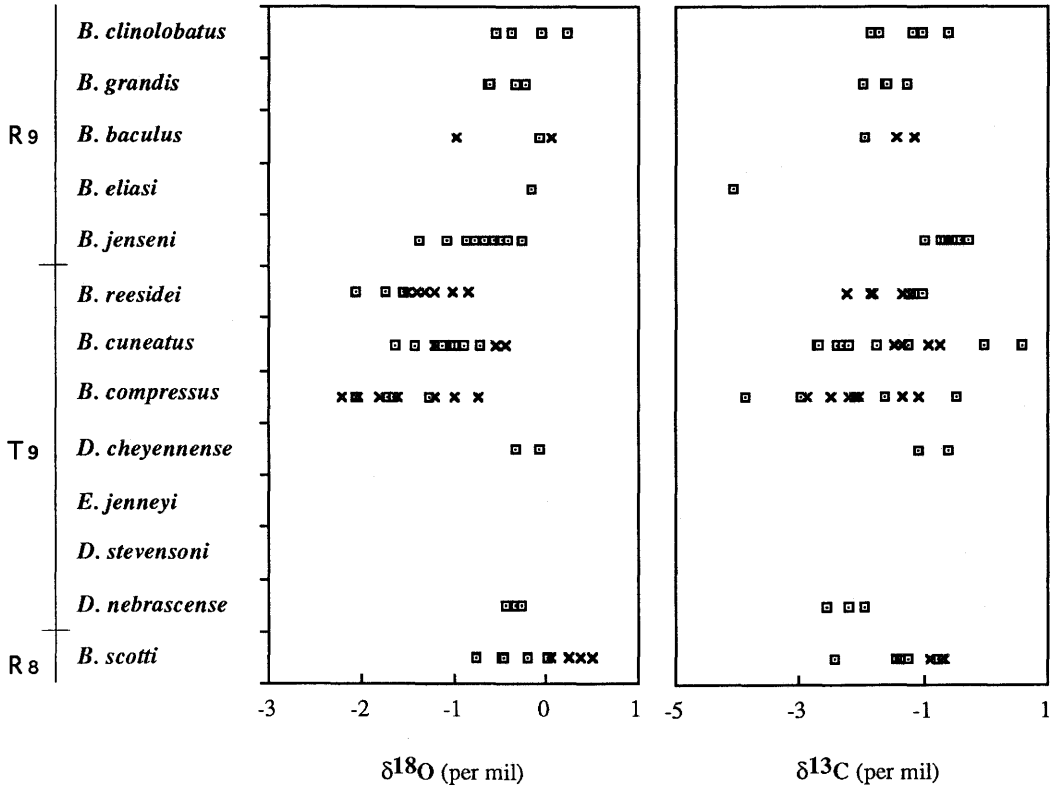


Fig. 4.2 $\delta^{18}O$ and $\delta^{13}C$ values in aragonite of baculitid shells from all the ammonite zones of the Bearpaw cyclothem. The samples were collected from places in the central portion of the Western Interior Basin. "▫" and "×" represent the samples from the United States and Canada, respectively. For the ammonite genera, *B.* = *Baculites*, *D.* = *Didymoceras*, *E.* = *Exiteloceras*. T9 and R9 represent the transgressive and regressive phases of the Bearpaw cyclothem respectively; R8 represents the regressive phase of the Claggett cyclothem.

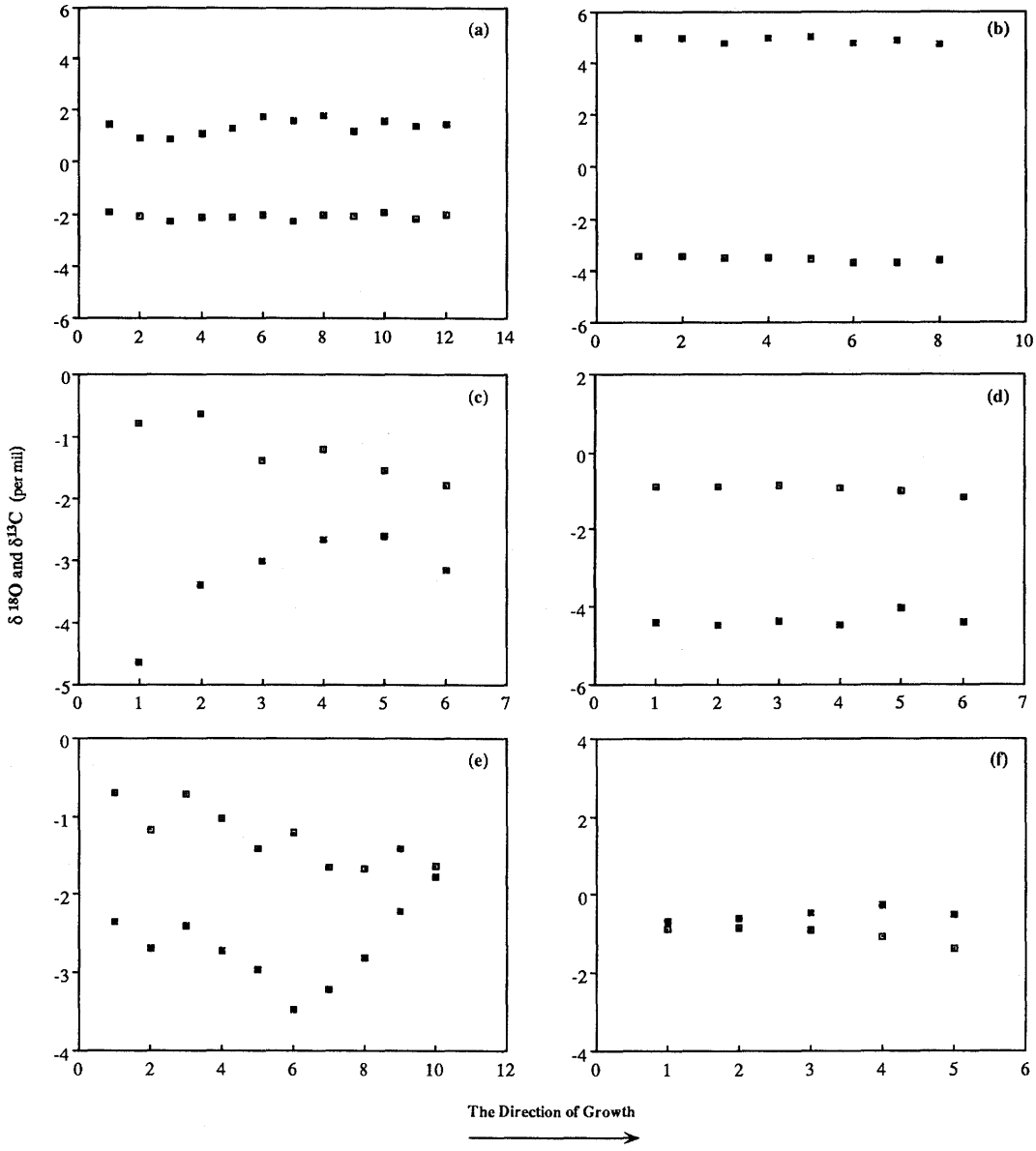


Fig. 4.3 Variations in the $\delta^{18}O$ and $\delta^{13}C$ values along the direction of growth of molluscan shells from the Bearpaw cyclothem: **(a)** Specimen DN(a) - *Didymoceras nebrascense*; **(b)** Specimen DC(a) - *Inoceramus sublaevis*; **(c)** Specimen BS(g) - *Menuites*; **(d)** Specimen BCN(e) - *Baculites cuneatus*; **(e)** Specimen BCN(a) - *Baculites cuneatus*; **(f)** Specimen BJ(a) - *Baculites jenseni*. Open squares represent $\delta^{18}O$ values and solid squares represent $\delta^{13}C$ values respectively. The data are from Table 4.1. The increasing numbers along horizontal axes refer to distances of the samples analysed from the starting point in the direction of growth, measured in cm.

4.3 Discussion and Implications

4.3.1 Vital effect

Many molluscan shells appear to be precipitated in isotopic equilibrium with the ambient water, and their stable-isotope compositions have been widely used as paleoenvironmental indicators (Epstein *et al.*, 1953; Milliman *et al.*, 1974; Savin, 1982; Kyser *et al.*, 1993). It must be conceded, however, that the variations in the stable-isotope compositions among co-existing molluscan fossils from the Bearpaw cyclothem could be caused by disequilibrium precipitation of their carbonate shells. Although many biogenic carbonates are precipitated in stable isotopic equilibrium with ambient waters, disequilibrium fractionation of oxygen- and carbon-isotopes during shell calcification in some marine organisms is well-documented (Goreau, 1977; Erez, 1978; Swart, 1983; Grossman, 1987; McConnaughey, 1989a, 1989c; Carpenter and Lohmann, 1995). The study by Mitchell *et al.* (1994) shows that some of molluscan fossil species from Plio - Pleistocene sediments in New Zealand and some Holocene species from the west coast of Scotland exhibit varying disequilibrium precipitation of carbonate shells with the seawater in which they lived. Skeletal aragonite from freshwater bivalves has also been found to be out of stable isotopic equilibrium with ambient water (e.g., Dettman and Lohmann, 1993; Fastovsky *et al.* 1993). Carbonate shells of molluscs, therefore, may not always be precipitated in equilibrium with their ambient waters, and in such cases stable-isotope analyses may be unreliable for interpreting prevailing paleoenvironmental conditions. Given the physical complexities of molluscs, varying degrees of disequilibrium precipitation likely exist in some of them.

Isotopic disequilibrium may be due to "metabolic isotope effects" or "kinetic

isotope effects" (both referred to as "vital effects") which are inherent in fast-growing shells or specific areas of shells. McConnaughey (1989a) argued kinetic isotope effects or kinetic fractionation probably occurs in most animals with calcareous skeletons because of their relatively fast growth rates. Kinetic fractionation takes place during hydration and hydroxylation of CO_2 in the process of shell calcification, involving discrimination against heavy oxygen and carbon isotopes. Lighter isotopes react more readily, leading to the formation of isotopically light HCO_3^- in the extracytoplasmic calcifying fluid (ECF) from which the carbonate is precipitated. During precipitation, however, movement of CO_2 and HCO_3^- across the boundary membrane from the cells to the ECF, and from the outside environments to the ECF, may occur at a rate that allows simultaneous equilibrium of both carbon and oxygen isotopes in solution in the ECF with the external medium. Therefore, the carbonate that precipitates more slowly should be closer to the equilibrium values. If precipitation is rapid, the carbonate will be isotopically light, far from being in equilibrium. The degree of disequilibrium will depend upon the rate of growth of the carbonate crystals. Different parts of the skeletal structure may have different rates of growth. Consequently, disequilibrium may lead to a range of stable-isotope values and strong linear correlations between $\delta^{18}O$ and $\delta^{13}C$ values of the carbonate shells. Such linear relationships between $\delta^{18}O$ and $\delta^{13}C$ values have been reported for corals (Land *et al.*, 1975; Erez, 1977 and 1978; McConnaughey, 1989c), some foraminifera (e.g., Duplessy *et al.*, 1981; Erez and Honjo, 1981), *Nautilus* (Eichler and Ristedt, 1966; Cochran *et al.*, 1981; Taylor and Ward, 1983), and calcitic algae (Keith and Weber, 1965).

Metabolic effects are usually considered to influence carbon-isotope composition,

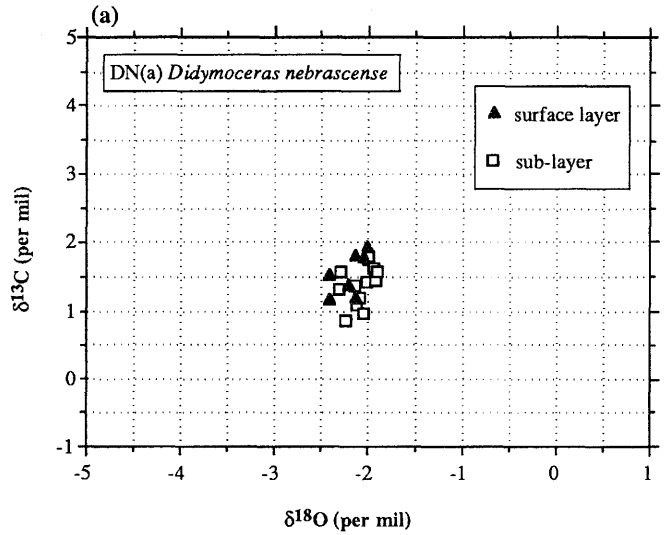
apparently arising from changes in the $\delta^{13}C$ values of the dissolved inorganic carbon (DIC) in the reservoir from which the skeleton precipitates (Swart, 1983; McConnaughey, 1989a). Metabolic effects on stable isotopes may result in either positive or negative values. Respiration should decrease, and photosynthesis should increase skeletal $\delta^{13}C$ values by selective addition or removal of ^{12}C, respectively. Jones *et al.* (1986) and McConnaughey (1989a) noticed that both photosynthetic and non-photosynthetic organisms have similar ranges of $\delta^{18}O$ values, and they postulated that skeletal $\delta^{18}O$ values do not have any direct connections to photosynthesis or respiration. Respired CO_2 will exchange oxygen isotopes with water, which would make the oxygen-isotope ratio of respired CO_2 indistinguishable from that of environmental CO_2. Most calcareous organisms have abundant carbonic anhydrase, an enzyme which catalyses oxygen-isotope exchange between CO_2 and water (Silverman, 1975). However, many studies (e.g., Erez, 1978; Grossman, 1987; Carpenter and Lohmann, 1995) show that metabolic CO_2 is enriched in both ^{12}C and ^{16}O, and thus metabolic effects also cause simultaneous lowering of both oxygen- and carbon-isotope values of carbonate shells relative to isotopic equilibrium. The linear trends of $\delta^{18}O$ and $\delta^{13}C$ values of calcite from respiratory organisms have slopes of 1.5 to 3.0 (Carpenter and Lohmann, 1995), whereas the linear trends of kinetic fractionation have slopes of 1.3 to 4.5 (McConnaughey, 1989b; Clark *et al.*, 1992). This may imply that the kinetic fractionation processes are operative during the precipitation of carbonate shells in respiratory organisms. Based on these observations, Carpenter and Lohmann (1995) suggested that the higher metabolic activity may be linked to a larger kinetic fractionation of both carbon and oxygen isotopes during hydroxylation of CO_2 or rapid

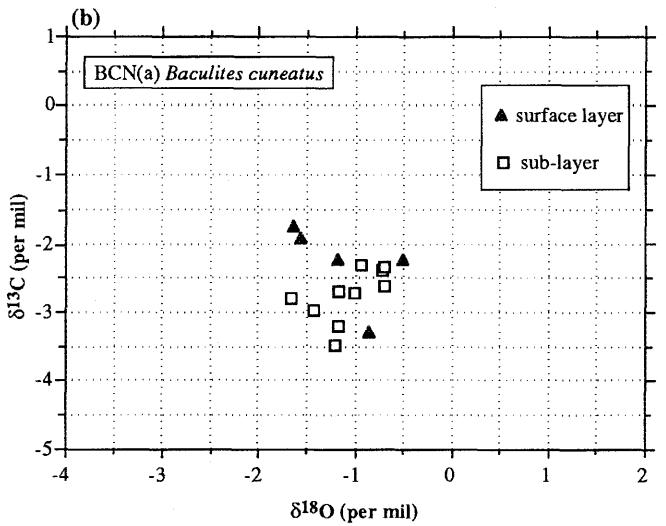
precipitation of calcium carbonate.

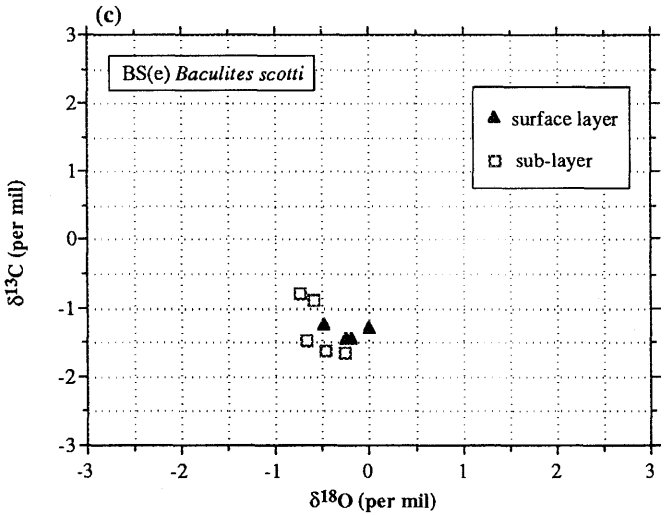
The stable-isotope compositions of the ammonites, bivalves, and other molluscan shells from the Bearpaw cyclothem are not consistent with the patterns of stable-isotope values produced by disequilibrium fractionation during shell calcification as a result of the kinetic or metabolic effects discussed above. Multiple analyses of different parts of single shells of ammonites and inoceramids do not show any linear relationship between $\delta^{18}O$ and $\delta^{13}C$ values. In contrast, the values exhibit clustered or randomly scattered distributions (Fig. 4.4 a to d). Figure 4.4 e to h show the relationship between the $\delta^{18}O$ and $\delta^{13}C$ values in shells of different molluscan species from the same locality and, therefore, from the same ammonite zone. Rather than the linear covariance of $\delta^{18}O$ and $\delta^{13}C$ values resulting from kinetic factors observed among modern brachiopods (Carpenter and Lohmann, 1995), co-existing molluscan fossils from the Bearpaw cyclothem exhibit different characteristics between the $\delta^{18}O$ and $\delta^{13}C$ values. Inoceramids have the highest $\delta^{13}C$ values but the lowest $\delta^{18}O$ values, whereas co-existing baculitids have the lowest $\delta^{13}C$ values but the highest $\delta^{18}O$ values. If these molluscs deposited their carbonate shells in isotopic disequilibrium with ambient waters, the shells with the greatest kinetic fractionation should have the lowest $\delta^{18}O$ and $\delta^{13}C$ values, whereas those with higher $\delta^{18}O$ and $\delta^{13}C$ values should have been deposited under conditions closer to equilibrium.

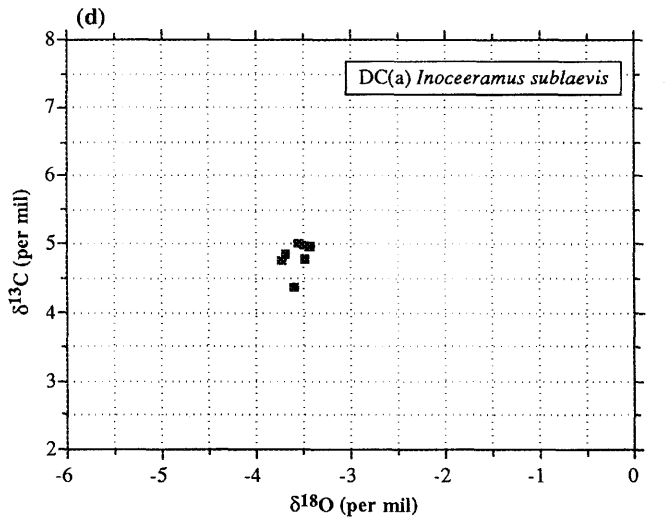
It has been reported that symbiotic algae can influence the stable-isotope compositions of corals and foraminifera (Erez, 1978; Cummings and McCarthy, 1982; Swart, 1983; McConnaughey, 1989a). Baculitids, inoceramids, and other molluscs in the Bearpaw sea probably also hosted symbionts, which could have affected the stable-

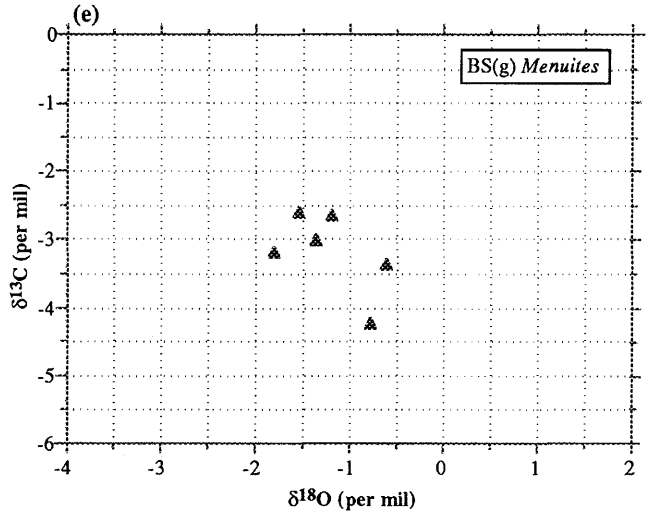
Fig. 4.4 Relations between $\delta^{18}O$ and $\delta^{3}C$ values of single molluscan shells from the Bearpaw cyclothem: (a) DN(a), *Didymoceras nebrascense* from the *D. nebrascense* Zone; (b) BCN(a), *Baculites cuneatus* from the *B. cuneatus* Zone; (c) BS(e), *Baculites scotti* from the *B. scotti* zone; (d) DC(a), *Inoceramus* sublaevis from the *D. cheyennense* Zone; (e) BS(g), *Menuites* from the *B. scotti* Zone; (f) Two *Baculites jenseni* BJ(a) and BJ(b) from the *B. jenseni* Zone; (g) *Inoceramus sublaevis* (DC(a)), *Baculites sp.* (DC(e)), and *Didymoceras cheyennense* (DC(b)) from the D. *cheyennense Zone*; (h) *Didymoceras nebrascense* (DN(a)) and *Baculites sp.* (DN(c)) from the *D. nebrascense* Zone. 'Surface layer' refers to samples from the uppermost part of the aragonite layer and 'sub-layer' refers to samples from the lower part of the layer. The data are from Table 4.1.

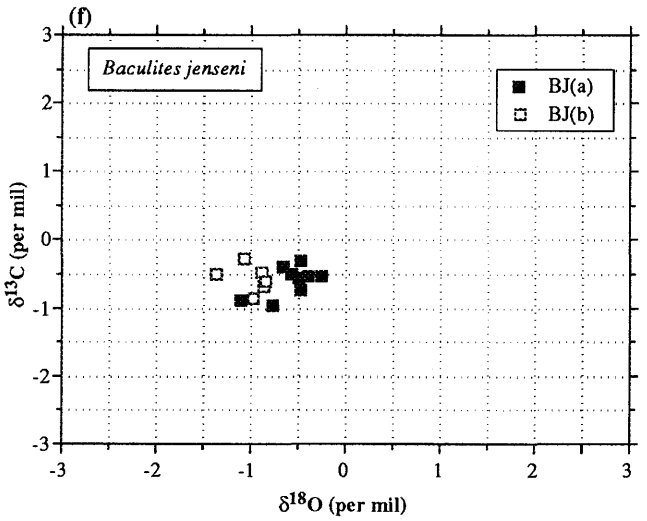

(a)
DN(a) Didymoceras nebrascense
surface layer
sub-layer
δ13C (per mil)
δ18O (per mil)

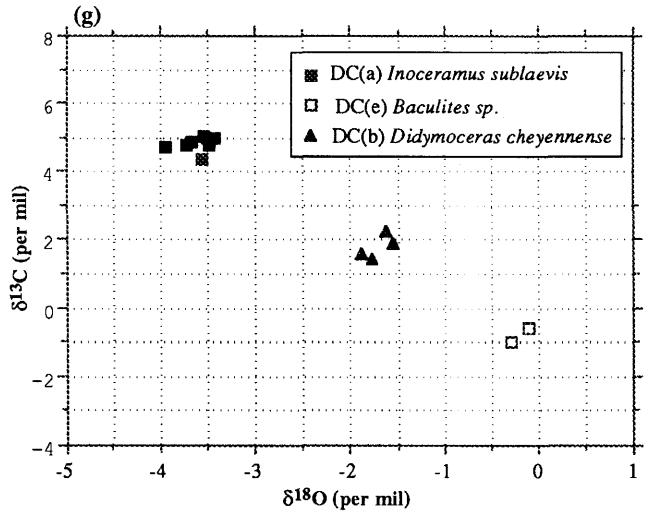

(b)
BCN(a) Baculites cuneatus
surface layer
sub-layer
δ13C (per mil)
δ18O (per mil)

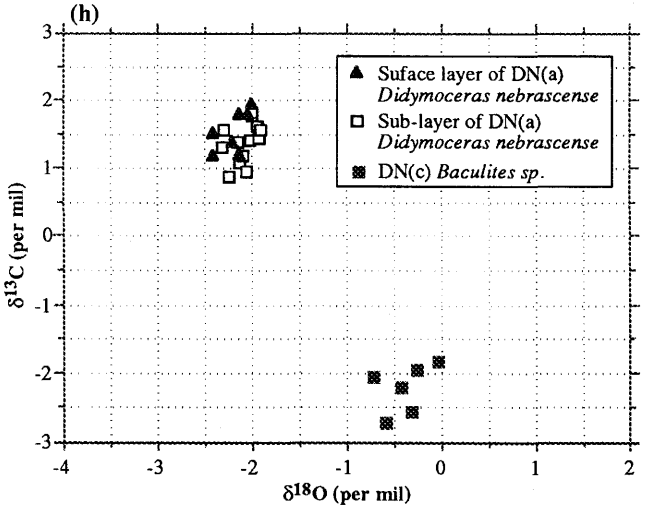

(c)
BS(e) Baculites scotti
surface layer
sub-layer
δ13C (per mil)
δ18O (per mil)


(d)
DC(a) Inoceeramus sublaevis
δ13C (per mil)
δ18O (per mil)


(e)
BS(g) Menuites
δ13C (per mil)
δ18O (per mil)


(f)
Baculites jenseni
BJ(a)
BJ(b)
δ13C (per mil)
δ18O (per mil)


(g)
DC(a) Inoceramus sublaevis
DC(e) Baculites sp.
DC(b) Didymoceras cheyennense
δ13C (per mil)
δ18O (per mil)


(h)
Suface layer of DN(a)
Didymoceras nebrascense
Sub-layer of DN(a)
Didymoceras nebrascense
DN(c) Baculites sp.
δ13C (per mil)
δ18O (per mil)

isotope compositions of their carbonate shells. This is especially true for the $\delta^{13}C$ values, because photosynthesis of symbiotic algae should increase $\delta^{13}C$ values of the molluscan shells by selective removal of ^{12}C. Photosynthetic symbiosis, however, depends on light intensity and should be a function of depth. Fairbanks and Dodge (1979) pointed out that the $\delta^{13}C$ values of coral skeleton decrease with depth, approximately following the relative light-intensity curve. Inoceramids were benthonic animals, and if symbiotic algae did affect the $\delta^{13}C$ values of molluscan shells, the values of inoceramid shells should be the least affected among the molluscs studied. The high $\delta^{13}C$ values of inoceramid shells from the Bearpaw sea argues against a normal photosynthetic symbiotic effect for these molluscs.

Unreasonably high-temperatures for the Bearpaw sea, calculated from the $\delta^{18}O$ values of inoceramid shells and assuming a $\delta^{18}O$ value of 0.0 ‰ for the seaway, led Tourtelot and Rye (1969) to postulate that these bivalves may have kinetically fractionated oxygen isotopes. Later, however, Sommer and Rye (1978) developed a rather insensitive oxygen-isotope geothermometer for aragonite and calcite using stable isotopic data from modern benthonic foraminifera, and applied this to Tourtelot and Rye's (1969) data to propose isotope equilibrium temperatures of 14^0C to 19^0C for aragonite and calcite layers of Bearpaw inoceramids (Sommer and Rye, 1978). Saltzman and Barron (1982) analysed stable isotopes of inoceramid shells from the Late Cretaceous open oceans, using cores obtained during the Deep Sea Drilling Program, and calculated temperatures of between 5^0C to 16^0C for a $\delta^{18}O$ value of seawater of -1.0 ‰. These are reasonable temperatures for open-ocean bottom waters. Wright (1987) determined that inoceramids and two other genera of epibenthonic bivalves from

the Bearpaw cyclothem have stable-isotope compositions similar to those from the open oceans. These data indicated that the stable-isotope compositions of the carbonate shells are likely a fair reflection of those of the environment which they shared, and that there were probably no species-related vital effects.

Given that vital effects appear to have been minimal for ammonites and inoceramids in the Bearpaw sea, a simple explanation of the heterogeneity in stable-isotope compositions of co-existing molluscan fossil shells could be that the baculitids, scaphitids, and other ammonites lived in different environments, but were transported to the same area in the basin only after death. However, the molluscan fossils in the Bearpaw Formation and its equivalents are commonly found grouped in small to large clusters of one or two genera, randomly orientated, and lacking abrasion (Caldwell, 1968; Wright 1987). They appear to be preserved essentially *in situ*, and to be not obviously allochthonous.

Rye and Sommer (1980) noticed that adult and juvenile ammonites are found together in the Western Interior Basin. They suggested that baculitids could have spent most of their life in open oceans and entered the seaway only to breed. If this were true, baculitids could be expected to be concentrated near the northern and southern apertures of the seaway. However, paleontological studies (Kauffman, 1984; Kauffman *et al.*, 1993) indicate that the mollusc-dominated macro-fauna of the Cretaceous Western Interior Basin shows significant endemism, which has been used to define paleobiogeographic subprovinces and their ecotones. Ammonites are most common in the mid-basin, and their number and diversity decrease toward the apertures of the basin. Moreover, the suggested migration of ammonites into the basin is contradicted by their

stable-isotope signatures. If ammonites had spent most of their life in the open oceans, their stable-isotope compositions would reflect that environment, not the environment of the seaway itself. Through most of the Late Cretaceous Epoch, the stable-isotope compositions of the ammonites found in deposits of the former seaway are different from those of the coeval open oceans (Kyser *et al.*, 1993). The $\delta^{18}O$ values of ammonites from the seaway increased toward the end of the Cretaceous Period, implying that the seaway probably had less restricted connections with the open oceans and that its waters were closer to "normal" open ocean and sea waters. Adult ammonites do not have significantly different stable-isotope compositions from juvenile ammonites found in the same zone (Whittaker, 1989), and therefore presumably lived in the same kind of environment.

It may be concluded, therefore, that the ammonites and inoceramids from the Bearpaw sea precipitated their shells essentially in stable isotopic equilibrium with the seawaters in which they lived, and that their isotopic values are a reliable indicator of paleoenvironment. This accords with many of the ammonites and inoceramids being autochthonous and endemic to the seaway. The stable-isotope compositions of their shells should represent those of the seaway during the Bearpaw cyclothem. Variable paleoenvironmental conditions, rather than vital effects, would therefore account for the heterogeneity in stable-isotope compositions among the co-existing molluscs from the Bearpaw cyclothem

4.2.2 Mode of life of ammonites

Stable-isotope compositions of co-existing inoceramids and baculitids are distinct

(Fig.4.1), implying that they lived in isotopically distinct environments within the seaway during the Bearpaw cyclothem. Inoceramids are known to have been benthonic, and therefore baculitids could have hovered and swam mostly in a higher part of the water column. This is consistent with paleontological considerations (Klinger, 1981). Except for the very early growth stage, the shell of a baculitid is straight or slightly curved throughout, without strong decoration. From a purely hydrodynamic point of view, this fairly smooth, straight, orthoconic shell has a low drag coefficient and is considered to have been capable of relatively rapid movement through the water compared to other ammonites. This implies that baculitids were probably effective nektonic animals.

Most ammonites appear to have the anaptychi and aptychi, the jaw apparatus, which suggests that baculitids may have moved to the bottom of the sea to feed (He *et al.*, 1996). This argument, however, is not supported by either hydrodynamic considerations or the stable-isotope compositions of the baculitid shells from the Bearpaw cyclothem. If baculitids had gone to the bottom for food, they would have to have been fast swimmers, like modern fish, otherwise they would have spent most of their time moving up and down the water column everyday, before and after feeding. Although ammonites with orthoconic shells, such as baculitids, were probably relatively fast swimmers relative to other ammonites, their deficiency in propulsion probably rendered them slow swimmers compared to fishes and endocochliates (Chamberlain, 1981). This deficiency is partly attributable to their shells. Ammonites maintain large phragmocones, which likely caused additional drag because of the shell being larger than necessary. Fish and other modern fast swimmers do not have this problem because they lack heavy protective structures. Their buoyancy needs can be easily satisfied by small

organs like air bladders, which are an effective use of space. Rapid swimming or movement among molluscs also depends on rapid reduction of mantle cavity volume, which is accomplished by contraction of the powerful retractor muscles that roof the mantle cavity. The retractor muscles of ammonites appear not to have roofed the mantle cavity, suggesting an ineffective and relatively weak jet propulsion system (Kennedy and Cobban, 1976). Therefore, although ammonites had a highly developed nervous system and a corresponding speed of reaction, the lack of power in the jet propulsion mechanism and the large inert bulk of the shell made rapid movement highly unlikely or impossible. Passive vertical migration, wherein vertical movement is induced by altering the amount of fluid in their phragmocones, is another widely accepted means of locomotion for ammonites and other ectocochliates (Chamberlain, 1981). However, due to the remarkably low permeability coefficient of the siphuncular tube, the speed of this kind of buoyancy-induced locomotion seems likely to have been even slower than jet propulsion (Chamberlain, 1981). Therefore, no matter what method of locomotion was used by baculitids, they were probably very slow and inefficient at vertical movement, even compared to the modern *Nautilus*. Hence, baculitids very probably did not go to the bottom for food; they probably fed on plankton or other ammonites much of the time (Chamberlain, 1981).

If baculitids did go to the bottom to feed, stable-isotope compositions along the growth direction of their shells should reflect this movement, as the water near the bottom had a different stable-isotope composition from that of the upper water column according to the difference in isotopic values of coexisting baculitids and inoceramids. For most baculitids, variations in the stable-isotope compositions along the growth

direction are very small (about 0.5 ‰) -- see Table 4.1 and Figure 4.3. Only a few have larger variations in $\delta^{18}O$ value of ca. 1.0‰. Seasonal temperature fluctuations are likely to be responsible for these kinds of variations. Most of the oceans of the world have annual ranges of surface temperature less than 5^0C (Lamp, 1972), which correspond to ca.1.0 ‰ variation in $\delta^{18}O$ value of minerals deposited in the oceans. Annual ranges exceeding this are confined to a few land-locked seas. During the Late Cretaceous Epoch, the Earth was much warmer and the temperature gradient lower than it is today (Savin, 1982). Consequently seasonal variations in surface temperature of the Cretaceous oceans would also be lower. This implies that changes in the $\delta^{18}O$ values of single carbonate shells deposited in oceans, due to seasonal fluctuation during the Late Cretaceous Epoch, should be less than 1.0‰. Whittaker *et al.* (1987) reported a 2.8‰ difference in $\delta^{18}O$ values between the early and adult stages of two specimens of baculitids from the Lea Park Formation. This large variation suggests that they may have changed their mode of life from nektonic or possibly planktonic to benthonic in later life. However, this variation is uncommon for baculitids which appear to have had a very stable mode of life, probably swimming very slowly in the upper part of the water column. Due to their nektonic or possibly planktonic mode of life, baculitids are not limited by sedimentary facies. They are widely distributed in different rock types throughout the great part of the Cretaceous Western Interior basin (Kennedy and Cobban, 1976). This contributes to their being used as one of the basis for establishing ammonite zones.

Three-dimensionally coiled heteromorph ammonites, such as *Didymoceras*, must have lived close to the bottom of the sea. In marked contrast to the baculitids, they have

stable-isotope compositions more like those of benthonic inoceramids, with low $\delta^{18}O$ values (-2.3 to -1.9 ‰) and high $\delta^{13}C$ values (0.9 to 1.8‰). It is not surprising that *Didymoceras* was a benthonic animal, considering the shape of its shell. The *Didymoceras'* shell is three-dimensionally coiled, lacking bilateral symmetry, and of much lower hydrodynamic efficiency than the baculitid shell. In addition, *Didymoceras* usually has a very long body chamber, indicating that buoyancy of the phragmocone may have been very low (Lehmann, 1981) because buoyancy for the active shell and animal is provided by the phragmocone. Therefore, *Didymoceras* probably led a predominantly benthonic life. Okamoto (1987) studied the possibilities of life orientation of three-dimensionally coiled heteromorph ammonites by computer simulation, concluding that a floating or lightly touching benthonic mode of life was most probable for these ammonites. *Didymoceras* probably spent most of its time swimming slowly, or floating, immediately, above the substrate. *Exiteloceras* has stable-isotope compositions similar to those of *Didymoceras,* and thus, presumably was also a benthonic animal. Compared to the other Bearpaw ammonites, scaphitids have more variable stable isotopic compositions, with some like those of *Didymoceras* but others in the range of baculitids. Based on stable-isotope compositions, therefore, scaphitids may have lived more or less throughout the main part of the water column.

In terms of general shape, *Didymoceras* and scaphitids belong to ammonite groups with ancylocones. They have a recurved, U-shaped body chamber at the adult stage, but virtually all types of coiling are know in their phragmocones. Different shapes of shell at the adult stage led Klinger (1981) to conclude that their mode of life in the early growth stage must have been different from that at the adult stage, as decreasing

excess weight resulted in the loosely coiled forms of the adult shell. This means that these ammonites may have led a nektonic or even planktonic mode of life at the adult stage. This kind of ontogenetic change is not reflected, however, in stable-isotope compositions; the adult shells of *Didymoceras* have $\delta^{18}O$ and $\delta^{13}C$ values close to those of benthonic inoceramids. It is possible that juvenile *Didymoceras* crawled on the sea bottom, carrying its shell in gastropod-like fashion, whereas, at the adult stage, it changed its mode of life to float immediately above the substrate. Furthermore, small variations in stable isotopic compositions of different growth stages of scaphitid shells suggest that these ammonites lived in the same part of the water column at both early and adult stages.

4.2.3 Paleoenvironmental implications

Differences among the stable-isotope compositions of coeval benthonic and nektonic or planktonic animals from the Bearpaw cyclothem points to the Bearpaw sea being isotopically stratified, in much the same way as were the older Claggett and Greenhorn seas (Whittaker *et al.*, 1987; Kyser *et al.*, 1993). Assuming a water temperature of 15^0C (see the following *4.2.4* and Appendix I for discussion), the upper part of the water column had $\delta^{18}O$ values of ca. -3.0 to -1.0 ‰ and $\delta^{13}C$ values of ca -5.0 to -1.0 ‰, as indicated by nektonic or planktonic baculitids. In contrast, the stable-isotope compositions of the benthonic inoceramids suggest that the waters near the bottom had much lower $\delta^{18}O$ values of ca. -6.0 to -4.0 ‰ and higher $\delta^{13}C$ values of ca. -0.0 to 4.0 ‰. Although convincing evidence exists for isotopic stratification of the seaway through much of the Late Cretaceous Epoch, the exact cause of this stratification

is unclear.

Tourtelot and Rye (1969) first reported differences in the stable isotopic compositions of coeval molluscs from the Upper Cretaceous Pierre Shale of Montana, Wyoming, and the Dakotas. Given a $\delta^{18}O$ value of 0.0 ‰ for the water in the seaway, the $\delta^{18}O$ values of the benthonic inoceramids used by Tourtelot and Rye (1969) would imply temperatures in excess of 40^0C, whereas the $\delta^{18}O$ values of their cephalopods would indicate more reasonable temperatures of ca. 20^0C. These temperature differences between the surface and bottom waters are the reverse of the normal distribution of temperatures, and hence densities, in the sea. Generally, surface waters are warmer than bottom waters, although this relationship may be reversed by local circulation. An inverse density stratification may have existed, but it would be unlikely to have persisted through much of the Late Cretaceous Epoch. In 1980, Rye and Sommer applied their empirical oxygen-isotope geothermometer for aragonite and calcite to Tourtelot and Rye's (1969) data and obtained equilibrium temperatures of only 14 to 19^0C for the inoceramid shells.

Influx of relatively ^{18}O-depleted fresh water to cause brackish-water conditions has been suggested to account for the lower $\delta^{18}O$ values of molluscan fossils. Scholle and Kauffman (1975) and Scholle (1977) examined the oxygen- and carbon-isotope compositions of both inoceramids and whole-rock samples from Cenomanian to Campanian rocks in the Western Interior Basin. Generally lower $\delta^{18}O$ values were found relative to those of coeval rocks in the European platform. They concluded, therefore, that lower $\delta^{18}O$ values in the Western Interior Basin probably were caused by low-salinity influxes rather than higher temperatures. Pratt (1983) also interpreted low $\delta^{18}O$

values of inoceramids and other bottom-dwelling organisms to have resulted from the presence of brackish waters in the Greenhorn sea of the Western Interior Basin. It follows, therefore, that the low $\delta^{18}O$ values of inoceramids and some ammonites (e.g., *Didymoceras*) from the Bearpaw cyclothem might also be due to similar brackish-water conditions. If the low $\delta^{18}O$ values of the seaway during the Late Cretaceous Epoch resulted from the presence of brackish water, the more $\delta^{18}O$-rich and, presumably, denser and more saline waters in which the baculitids lived would have overlain the brackish and lighter bottom waters. As discussed above, such a density stratification would have been unstable and therefore, unlikely to persist.

Wright (1987) studied the stable-isotope compositions of molluscan fossils from the Upper Cretaceous Pierre Shale in the United States and devised a modified model to explain isotopic stratification of the Late Cretaceous seaway. She postulated that fluvial run-off from the western highlands spread eastward, forming a low-salinity cap on the surface of the seaway. The surface water was decoupled from the underlying water and subsequently modified by evaporation on the eastern margin of the seaway until its density increased sufficiently to force sinking and a counter flow of modified low-salinity or brackish water westward along the bottom of the seaway. Although this low-salinity cap may have existed from time to time for short periods, it is unlikely to have done so through all of Late Cretaceous time. In the short term, storms and waves presumably would have disrupted it. In the longer term, Wright's model places severe restrictions on boreal waters entering the seaway, which contrasts with paleontological evidence strongly supporting the introduction of these waters at times up to and including Late Campanian age (Caldwell, 1968; Gill and Cobban, 1973; Kauffman, 1975; Eicher and

Diner, 1985).

Another possible means of achieving isotopic stratification may have been through the modification of bottom waters by isotopic exchange between these waters and detritus near or at the bottom (Whittaker, 1989; Kyser *et al.*, 1993). O'Neil and Kharaka (1976) and James and Baker (1976) proposed that oxygen-isotope exchange may accompany cation exchange between detrital clays and seawater. Stable-isotope exchange between pore water and volcanic ash during alteration of the ash to smectite would result in low $\delta^{18}O$ values of the pore water. The conversion of volcanic glass with an initial $\delta^{18}O$ value of +7‰ to a clay mineral with a $\delta^{18}O$ value near +25‰ would produce pore water with low $\delta^{18}O$ values, similar to those of the shells of the benthonic organisms from the Western Interior Seaway (Kyser *et al.*, 1993). The modified pore water may have diffused and been expelled from the sediments, possibly enhanced by bioturbation, which would have affected the sessile benthonic organisms (e.g., inoceramids) more than the mobile benthonic animals (e.g., *Didymoceras)*.

Variations in $^{18}O/^{16}O$ ratios of baculitid shells in relation to biostratigraphic sequence could be due to changes in the temperature, the $^{18}O/^{16}O$ ratios of the seawater or both in which the organisms lived. The volume of continental ice and influx of fresh water are the two main factors that could have affected the $^{18}O/^{16}O$ ratio of the water in the seaway. Other factors are likely to have been negligible or only locally important. Change in volume of continental ice is potentially the most important factor because ice in polar areas have much more negative $\delta^{18}O$ values than modern seawater (Shackleton and Kennett, 1975). Paleoenvironmental data suggest, however, that there was no, or negligible, continental ice during the Late Cretaceous Epoch (Savin, 1982; Frakes, 1979;

Upchurch and Wolfe, 1993). If a polar continental ice cap existed, then it was probably restricted to the core of the Antarctic land mass. In the Arctic region, the temperature of the waters has been estimated to have been about 12^0C (Kauffman, 1975,1977). Hence, either influx of fresh water into the seaway or change in temperature with time is more likely to have accounted for the variations in stable-isotope values of the baculitid shells.

Influx of fresh water, however, is irreconcilable with the patterns of change in the $\delta^{18}O$ values of the baculitid shells with biostratigraphic sequence. Generally, the baculitids with the lowest average $\delta^{18}O$ values are from the *B. reesidei* and *B. compressus* zones, with baculitids from the B. *jenseni* and B. *cuneatus* zones also yielding lower $\delta^{18}O$ values than those of other zones. These four zones span the time when transgression of the Bearpaw sea was at its peak or near peak (Caldwell, 1968; Gill and Cobban, 1973), and therefore, the time when marine environmental conditions would have been most typically open sea. If influx of fresh water into the seaway was significant during the Bearpaw cycle, one would have expected it to have been strongest during the times denoted by the other older and younger ammonite zones rather than those corresponding to peak transgression. The baculitid shells from these older and younger zones then should have the more negative $\delta^{18}O$ values because the seaway was narrower during these times and tectonic deformation more active along the western margin. In contrast, the oxygen-isotope compositions of the zonal baculitids from the regressive and early transgressive phases are very close to those of fossils from the contemporary open oceanic environments (Shackleton and Kennett, 1975; Kyser *et al.*, 1993). The baculitids from the *D. stevensoni* Zone in Wyoming have lower $\delta^{18}O$ values than those of coeval baculitids from near the centre of the basin (Table 4.1). The *D.*

stevensoni Zone spans the time of earliest transgression of the Bearpaw sea, and Wyoming then lay near to shore (Gill and Cobban, 1973; Cobban *et al.*, 1993). The surface water of the Wyoming region could then have been contaminated by fresh waters from local rivers only. Paleontological evidence, in general, suggests that, during the whole Bearpaw cycle, most of the seaway was negligibly brackish if brackish at all. In contrast to the older cycles, the cheilostomate bryozoans -- fairly stenohaline organisms (Ryland, 1970) -- are fairly common throughout the upper Pierre Shale in the United States and are present in the Bearpaw Formation of the Southern Saskatchewan River valley (Gill and Cobban 1966; Caldwell, 1968). Corals have been found in sedimentary rocks from several parts of the Western Interior Basin (Gill and Cobban, 1966; Caldwell, 1968); and a rudist bivalve, *Ichthyosarcolites coraloidea* (Hall and Meek), was recovered from the Bearpaw Formation in southwestern Saskatchewan (Caldwell and Evans, 1963). All such evidence suggests that, during the Bearpaw cycle, the fresh-water influx into the seaway was relatively low and its effect on the stable-isotope compositions of the baculitids was insignificant. The variations in the stable isotopic compositions of the baculitids, therefore, are almost certainly a response to fluctuations in temperatures of the seaway. The lowest $\delta^{18}O$ values of baculitids occur in the middle of the biostratigraphic sequence, which was when the highest temperature of the seaway were realized during peak or near-peak transgression. The differences between the $\delta^{18}O$ values of different baculitids from the same ammonite zone reflect relatively small temperature fluctuations of the Bearpaw sea during each ammonite zone since these baculitids doubtless lived at different times during the temporal span of the zone. The similarity in stable-isotope compositions of molluscan fossils from the Canadian and

American portions of the basin supports the inference that temperature differences between them were minimal, such that the latitudinal temperature gradient was much lower during the Bearpaw cycle than it is in the oceans today (Kauffman, 1977; Savin, 1982).

Influx of fresh water includes precipitation and run-off from rivers. The apparent low influx of fresh water into the seaway during the Bearpaw cycle implies, therefore, that both precipitation and river run-off were low. The climate of the Western Interior Seaway, therefore, might well have been drier during the Bearpaw cycle than during previous Cretaceous cycles. This finds support in studies of the Cretaceous vegetation of the Western Interior (Upchurch and Wolfe, 1993). They have shown that, relative to the Cenomanian Age when precipitation was heavy, the remainder of the Cretaceous Period was relatively dry, especially at low-middle paleolatitudes.

Prevalence of somewhat brackish-water conditions in both surface and bottom waters has been considered one of the probable reasons for the poorly diversified, mollusc-dominated fauna of the seaway during the Late Cretaceous Epoch (Kauffman and Caldwell, 1993). As discussed, however, the stable-isotope compositions of the molluscs imply that any appreciable widespread, brackish water-conditions must have been very limited. Other environmental factors should be sought, therefore, to explain the rarity of the numerous groups of stenohaline organisms (sponges, bryozoans, brachiopods, corals and echinoderms) in the Bearpaw cyclothem relative to the contemporaneous faunas of the open seas covering non-epicontinental regions (the Gulf Coast, for example).

4.2.4 Paleotemperature of the Bearpaw sea

Paleotemperatures were calculated using the empirical temperature scale (Equation 4.1) developed by Grossman and Ku (1986), based on naturally occurring aragonitic foraminifera and molluscs in normal seawater:

$$T = 20.6 - 4.34\ (\delta_A - \delta_W) \qquad (4.1)$$

where T refers to temperature in ^0C, δ_A is the $\delta^{18}O$ value of aragonite relative to PDB, and δ_W is the $\delta^{18}O$ value of the ambient water relative to PDB.

In order to estimate paleotemperatures from the stable isotopic data of carbonates, the oxygen isotopic value (δ_W) of the ancient water inhabited by the organisms must be evaluated. Local variations in the δ_W due to salinity variations and global changes in the δ_W of ancient oceans must be taken into consideration to determine the $\delta^{18}O$ value of local seawater. The epicontinental sea of the Cretaceous Western Interior Basin had limited connection to the open oceans, even though it may have been relatively well connected during peak transgressive episodes. The stable-isotope composition in this restricted environment may have been more affected by local factors, such as precipitation, evaporation, and run-off from rivers. Variations in surface evaporation-precipitation give rise to variations in the isotopic compositions of seawater. The $\delta^{18}O$ value of precipitation becomes more negative with increasing latitude, and at present, in higher latitudes, where precipitation exceeds evaporation, the surface waters are isotopically lighter than mean ocean water. Due to lower temperature gradients during the Cretaceous Period (Kauffman, 1975; Savin, 1982), however, the effect of variation in the evaporation-precipitation balance on the $\delta^{18}O$ value of seawater can be ignored. As discussed above, influx of fresh water to the seaway probably was relatively

low during the Bearpaw cycle, and contamination of the seaway may well only have been local and confined to near-shore areas. Thus, the mean oxygen isotopic composition of open oceans can be used as an approximation for that of the Bearpaw sea.

The most likely processes that could have significantly affected the stable-isotope composition of the oceans are interactions between the oceanic crust and sea water, and continental glaciation. The oxygen-isotope composition of oceanic crust is intensively altered by exchange with seawater, both at high and low temperatures (Muehlenbachs and Clayton, 1976). However, the effects of these two alteration processes are opposite and so they effectively buffer the $\delta^{18}O$ value of the oceans (Gregory, 1991). Glaciation is thus the only known major factor controlling variation in the $\delta^{18}O$ values of the oceans in geological history. Ice now stored in polar areas has more negative $\delta^{18}O$ values than modern oceans, and consequently large-scale formation and melting of continental ice should strongly affect the $\delta^{18}O$ values of the oceans. As no significant permanent ice cover existed during the Late Cretaceous Epoch (see the previous discussion), the $\delta^{18}O$ value of the Cretaceous oceans must have been more negative than that of modern oceans. The overall average $\delta^{18}O$ value of ocean water today, in terms of PDB, is about -0.28 ‰ (Craig, 1965). Using a value of -50 ‰ for the $\delta^{18}O$ value of polar ice today (Shackleton and Kennett, 1975), the $\delta^{18}O$ value of the ocean prior to the formation of the presently existing ice sheets may be estimated at -1.28 ‰, which is used as the mean $\delta^{18}O$ value of the Bearpaw sea to calculate the temperatures of the seaway.

Because the bottom waters of the seaway were probably affected by isotope exchange between sediment and seawater, which is difficult to quantify, the temperatures of bottom-waters are not calculated. The variations in surface temperatures of the

Bearpaw sea, calculated from the oxygen isotopic compositions of the baculitids, are indicated in Figure 4.5. Assuming no variation in the $\delta^{18}O$ value of the Bearpaw sea, the surface temperature generally rose during transgression and fell after peak transgression. In the early transgressive phase (*D. nebrascense* and *D. stevensoni* times), the temperature was ca. 13 - 17^{0}C and increased toward the highest values typical of peak transgression. It remained nearly 20^{0}C through that period. In the following regressive phase, the temperature decreased to ca.14^{0}C at the end of the cycle (*B. clinolobatus* time).

To some extent, the temperature trend of the seaway during the Bearpaw cycle is probably related to CO_2 degassing from the increased tectonic activity and metamorphism west of the basin. These events likely increased the CO_2 in the atmosphere, consequently elevating the temperatures of the area. Towards the middle of the transgression, the proto-Lamaride orogeny intensified (Fig 1.3) due to the further collision of the American and Pacific plates, with subduction generating extensive metamorphism in the proto-Cordilleran region. Pelagic and slope carbonates, subducted beneath the continental plate, and carbonates in the orogeny underwent regional metamorphism. A fraction of the carbonates would be decomposed to produce a large volume of CO_2, released into the atmosphere through volcanism, fractures, and faults. It is postulated that this kind of degassing occurred in the early stages of the collision and orogeny, when the temperature was high enough to decompose carbonate minerals (Kerrick and Caldeira, 1993). Kerrick and Caldeira (1993) related the warmest climate during the Early Eocene Epoch to extensive CO_2 degassing from the Himalayan orogen through metamorphism. They demonstrated that decarbonation of large volumes

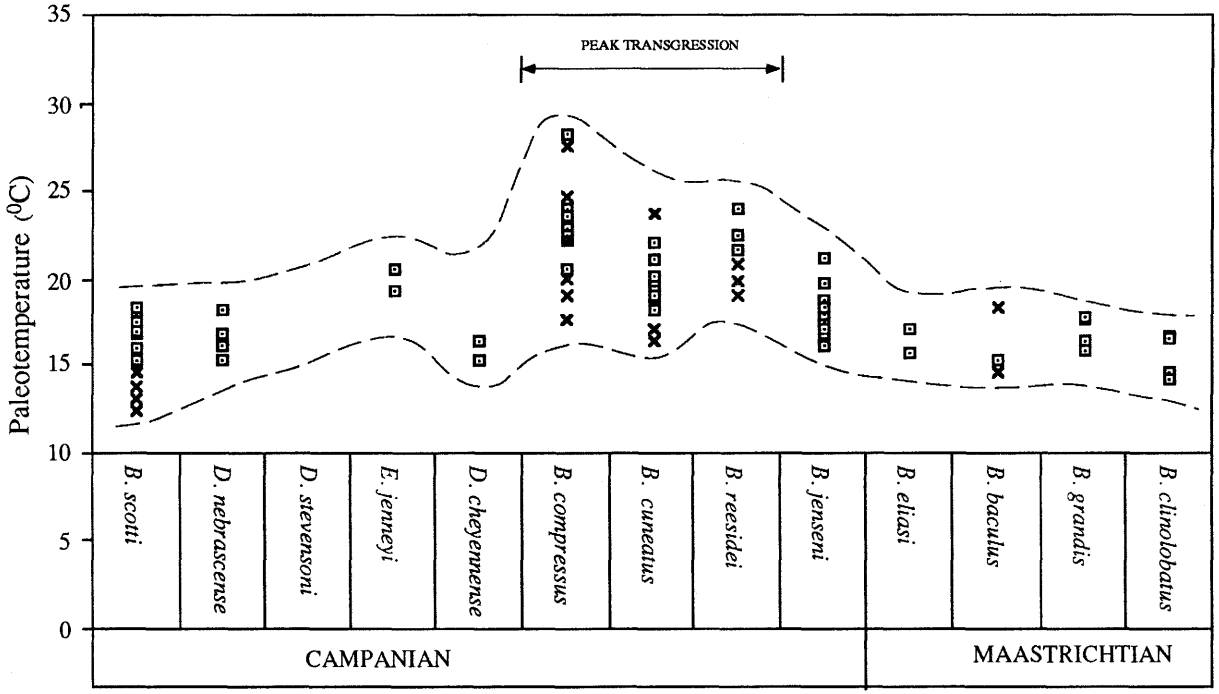


Fig. 4.5 Paleotemperature of the seaway during the Bearpaw cycle calculated from the $\delta^{18}O$ values of baculitid shells from the central portion of the Western Interior Basin, assuming the $\delta^{18}O$ value of the water in the seaway is -1.28 per mil. Abbreviations: *B.* = *Baculites*, *D.* = *Didymoceras*, *E.* = *Exiteloceras*. Stable isotopic data for calculation are from Table 4.1. " ▫" and " ×" refer to the samples from the United States and Canada, respectively. The Bearpaw sea reached peak transgression during *B. compressus*, *B. cuneatus*, and *B. reesidei* times according to Caldwell (1968), Gill and Cobban (1973), and Cobban *et al.* (1993).

of impure carbonates by rapid prograde metamorphism, and transportation of the CO_2 produced to the surface by fluids through volcanism, fractures, and faults, could have released up to 10^{19} moles of CO_2 into the atmosphere, causing a significant global warming. After the peak transgression of the Bearpaw cycle, the intensity of tectonic activity and the temperature of metamorphism probably decreased gradually, reducing the emission of CO_2 from the decarbonation of carbonates. Therefore, the temperature of the region also decreased, as seen in the temperature trend of the seaway during the Bearpaw cycle. The intensified tectonic activity expressed by increased volcanism is recorded by bentonites (originating as volcanic ashes produced during explosive eruptions) in the Bearpaw Formation and its equivalents. The numbers of bentonite beds increase in the transgressive hemicyclothem and decrease again in the regressive hemicyclothem (Kauffman and Caldwell, 1993).

4.3 Summary

The lack of a linear relationship between the $\delta^{18}O$ and $\delta^{13}C$ values in ammonite shells indicates that these animals deposited their shells essentially in isotopic equilibrium with the ambient waters in which they lived. Thus, the ammonites probably were not like other fast-growing and short-lived cephalopods; their larger body size was most likely due to longevity rather than fast growth of the shell. Stable-isotope compositions of the ammonite shells generally provide good records of the paleoenvironments of ancient oceans and seas.

Comparative study of the stable-isotope compositions of coexisting molluscan fossils suggests that ammonites could be planktonic or nektonic animals (e.g., *Baculites*),

the shells of which have the highest average $\delta^{18}O$ values and lowest average $\delta^{13}C$ values, and probably benthonic animals (e.g, *Didymoceras*), the shells of which have the lowest average $\delta^{18}O$ values and highest average $\delta^{13}C$ values, similar to the inoceramids. Differences in stable-isotope compositions among coeval ammonites and inoceramids imply that the waters within the seaway were isotopically stratified during the Bearpaw cycle. The bottom waters may have been modified by isotopic exchange with the sediments on the seafloor.

There is a clear relationship between biostratigraphic sequence and the $\delta^{18}O$ values of the baculitids from the Bearpaw cyclothem. The baculitids from zones spanning the peak transgression have the lowest average $\delta^{18}O$ values, whereas those from other zones have higher average $\delta^{18}O$ values. Changes in isotopic values through the zonal sequence suggest rising and falling temperatures during transgression and regression, respectively. Temperature fluctuations during the Bearpaw cycle may be partially related to intensified tectonic activity west of the basin. The pattern of the $\delta^{18}O$ values cannot be readily explained by variations in freshwater influx. The Bearpaw sea was not brackish, and thus, other environmental factors are responsible for the rarity of many invertebrate groups prevalent in coeval open oceans and seas.

5. TRACE-ELEMENT GEOCHEMISTRY OF MOLLUSCAN FOSSILS

5. 1 Introduction

Determination of the chemical compositions, and particularly the concentrations of trace elements, of the carbonate shells of organisms has become one of the most useful means of probing the chemistry of ancient oceans and seas, and hence of reconstructing paleoenvironmental conditions. The chemical and physical conditions of the ambient waters directly or indirectly control the major- and trace-element concentrations of the carbonate shells. Experimental studies show that an increase in Sr/Ca and Mg/Ca ratios in a solution produces a corresponding linear increase in Sr/Ca and Mg/Ca ratios in carbonate shells of molluscs and brachiopods, as well as in foraminiferal tests (Lowenstam, 1961; Zolotarev, 1974; Buchardt and Fritz, 1978; Lorens and Bender, 1980; Delaney *et al.*, 1985). It has also been demonstrated that carbonate shells record the trace-element compositions of the seawaters in which the shells were secreted (Boyle and Keigwin, 1985/86; Lea and Boyle, 1993; Russell *et al.*, 1994).

Factors significantly affecting the chemical composition of seawater may include the extent of continental weathering of igneous or carbonate rocks delivered into seas by streams, volcanic sediments deposited in basins, and hydrothermal circulation. Removal of elements from the sea through precipitation of minerals and recycling through diagenesis exert some control over the chemical composition of the seawater (Holland,

1978). These effects should impart predictable signatures to the seawater solute chemistry and thus to the chemical compositions of shells. It is likely that the Late Cretaceous polar and subtropical oceans, which invaded the seaway (Kauffman and Caldwell, 1993), had distinct chemical compositions. The mixing and modification of these two oceans during transgression of the seaway could be reflected in variations in chemical compositions of the molluscan fossils.

Some trace elements, such as Cr, V, U, Mo, and the rare earth elements Ce and Eu, have multiple valence states in sediments and waters near the Earth's surface (e.g., Calvert and Pedersen, 1993). Typically, they have different solubilities in oxygenated and oxygen-deficient seawater, and are partitioned between the solid and solution phases to different extents under different redox conditions. These elements, specifically Ce, have been proposed as tracers for the redox states of ancient oceans and seas (Wright *et al.*, 1984; Coveney *et al.* 1987, 1991; Calvert, 1990; Calvert and Pedersen, 1993). Information on the oxidation-reduction conditions of the seaway during the Bearpaw cycle, therefore, may be inferred by investigating trace elements in the carbonate shells of the molluscan fossils.

5. 2 Sample Locations and Distributions

Ammonites and other coeval molluscs lived at different depths in the water column of the seaway, and consequently their chemical compositions should record the paleoenvironmental conditions of the waters at these depths. Chemical compositions of the baculitids, which were nektonic to planktonic animals, should provide information on conditions in the upper part of the water column, whereas those of benthonic

inoceramids and didymoceratids should furnish data on the bottom-water conditions. Both nektonic and benthonic molluscs, if available, were selected from each of the ammonite zones of the Bearpaw cyclothem. Unlike the baculitids, only limited numbers of inoceramids could be used for chemical analysis due to their poor preservation in some ammonite zones. Most of the fossils used are from locations in the central part of the Western Interior Basin where conditions will reflect the basin as a whole. Near-shore waters are largely affected by local environmental factors, such as influx of stream waters, and thus fossils from near-shore localities should record such variations. Such location were thus avoided in this study. The information about the fossils used in the study is in Table 5.1.

5. 3 Major- and Minor-Elements

5.3.1 Results

Results of major- and minor-element compositions are given in Table 5.2. The data are reported in the form of element/Ca ratios, multiplied by a factor of 1000. These ratios in shells of benthonic and nektonic fossils are also plotted relative to the ammonite zones for variations within the biostratigraphic sequence (Fig. 5.1).

The Sr/Ca, Mn/Ca, Mg/Ca and Na/Ca ratios of aragonitic shells of nektonic baculitids generally do not vary much with respect to the biostratigraphic sequence throughout the Bearpaw cyclothem. An exception is specimen BB(d) from the *B. baculus* Zone which has anomalously high Mg/Ca and Mn/Ca ratios of 3.84 and 3.79, respectively. Compared to nektonic baculitids, shells of benthonic inoceramids and didymoceratids have more variable Sr/Ca, Mg/Ca, Mn/Ca and Na/Ca ratio, but their

Table 5.1 Sample descriptions of the molluscan fossils used for element analysis

Sample	Taxon	Mode of Life	Interval Zone	Location
BL(b)	*B. clinolobatus*	Nektonic	*B. clinolobatus*	Dewey, South Dakota
BG(d)	*B. grandis*	Nektonic	*B. grandis*	Pennington, South Dakota
BB(d)	*B. baculus*	Nektonic	*B. baculus*	Haakon, South Dakota
BE(c)	*B. eliasi*	Nektonic	*B. eliasi*	Crook, South Dakota
BE(b)	*Inoceramus sp.*	Benthonic	*B. eliasi*	Crook, South Dakota
BJ(a)	*B. jenseni*	Nektonic	*B. jenseni*	Huerfano, Colorado
BR(c)	*B. reesidei*	Nektonic	*B. reesidei*	Wyoming
BR(a)	*Inoceramus sp.*	Benthonic	*B. reesidei*	Wyoming
BCN(a)	*B. cuneatus*	Nektonic	*B. cuneatus*	Haakon, South Dakota
BCN(c)	*Inoceramus sp.*	Benthonic	*B. cuneatus*	Haakon, South Dakota
BC(b)	*B. compressus*	Nektonic	*B. compressus*	Pennington, South Dakota
DC(e)	*Baculites sp.*	Nektonic	*D. cheyennense*	Pennington, South Dakota
DC(a)	*Inoceramus sp.*	Benthonic	*D. cheyennense*	Pennington, South Dakota
EJ(b)	*scaphite*	Nektonic	*E. jenneyi*	Carter, Montana
EJ(a)	*Inoceramus sp.*	Benthonic	*E. jenneyi*	Carter, Montana
DS(c)	*Baculites sp.*	Nektonic	*D. stevensoni*	Albany, Wyoming
DS(b)	*Inoceramus sp.*	Benthonic	*D. stevensoni*	Albany, Wyoming
DN(c)	*Baculites sp.*	Nektonic	*D. nebrascense*	Fall River, South Dakota
DN(a)	*D. nebrascense*	Benthonic	*D. nebrascense*	Fall River, South Dakota
BS(d)	*B. scotti*	Nektonic	*B. scotti*	Fall River, South Dakota
BS(f)	*I. sublaevis*	Benthonic	*B. scotti*	Fall River, South Dakota

Note: I. = Inoceramus; D. = Didymoceras; B. = Baculites

Table 5.2 Element/Ca ratios in aragonite of selected molluscan shells from the Bearpaw cyclothem

Sample	Taxon	Na/Ca	Mg/Ca	Fe/Ca	Mn/Ca	Sr/Ca
BR(a)	*Inoceramus sp.*	5.97	1.35	1.93	1.32	7.80
BCN(c)	*Inoceramus sp.*	6.22	1.36	7.76	0.63	6.73
DC(a)	*Inoceramus sp.*	7.89	0.38	1.28	0.33	5.51
EJ(a)	*Inoceramus sp.*	6.77	0.46	1.72	0.50	5.71
DS(b)	*Inoceramus sp.*	5.63	1.98	4.22	3.32	6.85
DN(a)	*D. nebrascense*	5.83	0.16	0.48	0.09	7.39
BS(f)	*I. sublaevis*	5.93	0.21	1.44	1.50	7.93
BL(b)	*B. clinolobatus*	6.42	0.42	1.45	0.66	9.29
BG(d)	*B. grandis*	5.16	0.16	0.26	0.14	9.26
BB(d)	*B. baculus*	5.16	3.84	2.36	3.79	7.53
BE(c)	*B. eliasi*	6.08	0.44	0.59	0.27	9.98
BJ(a)	*B. jenseni*	5.17	0.26	3.14	0.19	7.98
BR(c)	*B. reesidei*	6.33	0.38	0.81	0.25	11.46
BCN(a)	*B. cuneatus*	5.89	0.22	1.57	0.20	6.67
BC(b)	*B. compressus*	5.26	0.49	1.32	0.36	8.04
DC(e)	*Baculites sp.*	7.14	0.26	0.96	0.07	7.99
EJ(b)	*scaphite*	5.58	0.76	4.33	0.76	10.61
DS(c)	*Baculites sp.*	4.78	0.51	2.93	1.24	9.13
DN(c)	*Baculites sp.*	5.73	0.26	1.88	0.09	6.68
BS(d)	*B. scotti*	6.32	0.25	1.07	0.14	7.31

Note: Element/Ca ratios are all multiplied by a factor of1000;
B. = Baculites; D. = Didymoceras; I. = Inoceramus;

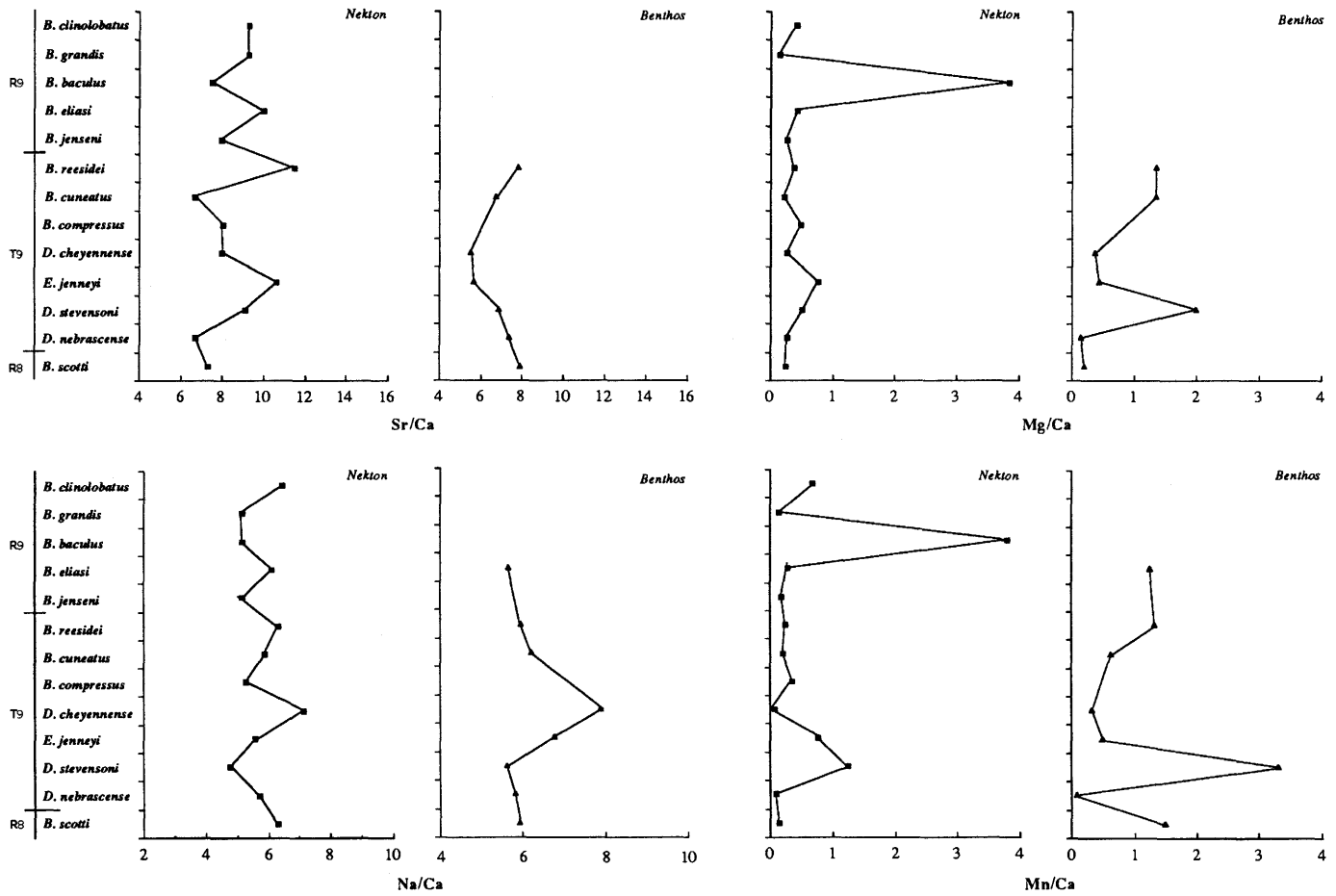


Fig. 5.1 Variations in the minor-element/Ca ratios of molluscan shells from the ammonite zones of the Bearpaw cyclothem. The significance of these ratios is explained in the text. The element/Ca ratios are all multiplied by a factor of 1000. For the ammonite genera, *B.* = *Baculites*, *D.* = *Didymoceras*, *E.* = *Exiteloceras*. T9 and R9 represent the transgressive and regressive phases of the Bearpaw cyclothem respectively; R8 represents regressive phase of the Claggett cyclothem (Gill and Cobban, 1966; Kauffman and Caldwell, 1993).

Sr/Ca (5.51 to 7.93) , Mg/Ca (0.10 to 1.98), and Na/Ca (5.63 to 7.89) ratios are generally less variable than their Mn/Ca (0.09 to 3.32) ratios.

5.3.2 Discussion

Molluscan organisms do not secrete their carbonate shells directly from the seawaters in which they live, but rather from the extrapallial fluid between the mantle and the inner shell surface (Saleuddin and Wilbur, 1983). Biogenic calcium carbonates are commonly considered to be in chemical disequilibrium with seawater because they have compositions different from those predicted on the basis of inorganic distribution coefficients (Lorens and Bender, 1980). Cells of the mantle presumably fractionate elements between the external medium and the extrapallial fluid. The concentration of metals in the extrapallial fluid may also be influenced by the binding properties of organic compounds in the extrapallial fluids (Saleuddin and Wilbur, 1983). A comparison of the concentration of inorganic ions in the external medium and extrapallial fluids, however, shows that in marine bivalves, the differences in the partition of Ca, Mg, Na, and K are small (Crenshaw, 1972; Wada and Fujinuki, 1976; Saleuddin and Wilbur, 1983), although concentrations of heavy metals are higher in the extrapallial fluids than in the external medium.

Laboratory culture experiments of molluscs and foraminifera indicate that the concentrations of both minor- and trace-elements in carbonate shells are mainly controlled by those in the external medium in which the shell are precipitated. Lowenstam (1961) showed that an increase in the Sr/Ca and Mg/Ca ratios in growth solutions elevates these ratios in brachiopod shells. Buchardt and Fritz (1978) and

Lorens and Bender (1980) reported a similar linear relationship between Sr/Ca and Mg/Ca ratios in growth solution and molluscan shells. The experimental study of Lorens and Bender (1980) also found that the relationship between elements in solution and in aragonitic shells is more direct than the one between elements in solution and in calcite shells, suggesting that aragonite from shells is a more reliable recorder of chemical conditions of paleoenvironments.

Temperature and growth rate of organisms are generally considered to have an insignificant effect on the partitioning of minor and trace elements between water and shell carbonates (Milliman *et al.*, 1974; Buchardt and Fritz, 1978). Delaney *et al.* (1985) postulated that generalized correlations between elements in foraminifera and temperatures may result from temperature-related factors, such as availability of food and light intensity rather than temperature alone. Temperature may affect growth rate; however, no relationship has been found between growth rate and minor- and trace-element concentrations of mollusc shells (Buchardt and Fritz, 1978; Lorens and Bender, 1980). Consequently, factors responsible for changes in the chemical composition of seawater should explain most of the variations of element/Ca ratios within shells of molluscs.

5.3.3 Paleoenvironmental implications

The relatively uniform Sr/Ca, Mg/Ca, Na/Ca, and Mn/Ca ratios in the aragonitic shells of baculitids, which were likely nektonic animals living in the upper part of the water column (see discussions in section 4), suggest a relatively stable chemical composition of the surface and near-surface waters of the seaway during the Bearpaw

cycle because baculitids. Smaller fluctuations in element/Ca ratios of nektonic fossil shells also imply that variations due to differential freshwater influx from run-off into the seaway was insignificant during the Bearpaw cycle. Riverine input from continental weathering into the seas and oceans is one of the primary factors that can affect the chemical composition of seawaters. The composition of the upper part of the water column should be more affected by run-off. The Bearpaw sea was somewhat narrowly constricted through a good part of the cycle, except peak transgression when it was well connected with the open oceans (Caldwell, 1968). Significant and variable influx of run-off into the seaway would have resulted in pronounced fluctuations in the chemical compositions of the sea, especially of the surface waters, and in sympathetic changes in element/Ca ratios of carbonate shells of the molluscs that lived in the seaway.

Variations in the influx of isotopically depleted river waters and in temperature, or some combination of these two, could have resulted in fluctuations of both the stable isotopic and chemical compositions of the seaway and consequently in those of the aragonitic molluscan shells. However, the absence of correlation between $\delta^{18}O$ values and Sr/Ca, Mn/Ca, Mg/Ca, and Na/Ca ratios in shells of nektonic baculitids (Fig. 5.2) is further evidence that variations in $\delta^{18}O$ values of aragonitic shells of baculitids are due mainly to fluctuations in the temperatures of the seaway rather than variable influxes of freshwater from rivers to the Bearpaw sea. Moreover, the low $\delta^{18}O$ values of benthonic faunal elements could not have resulted from brackish water, or evaporated brackish water, because if the influx of freshwater from run-off were significant, the chemical compositions of the surface waters would have been more variable rather than relatively stable through the biostratigraphic sequence. This supports the conclusion drawn from

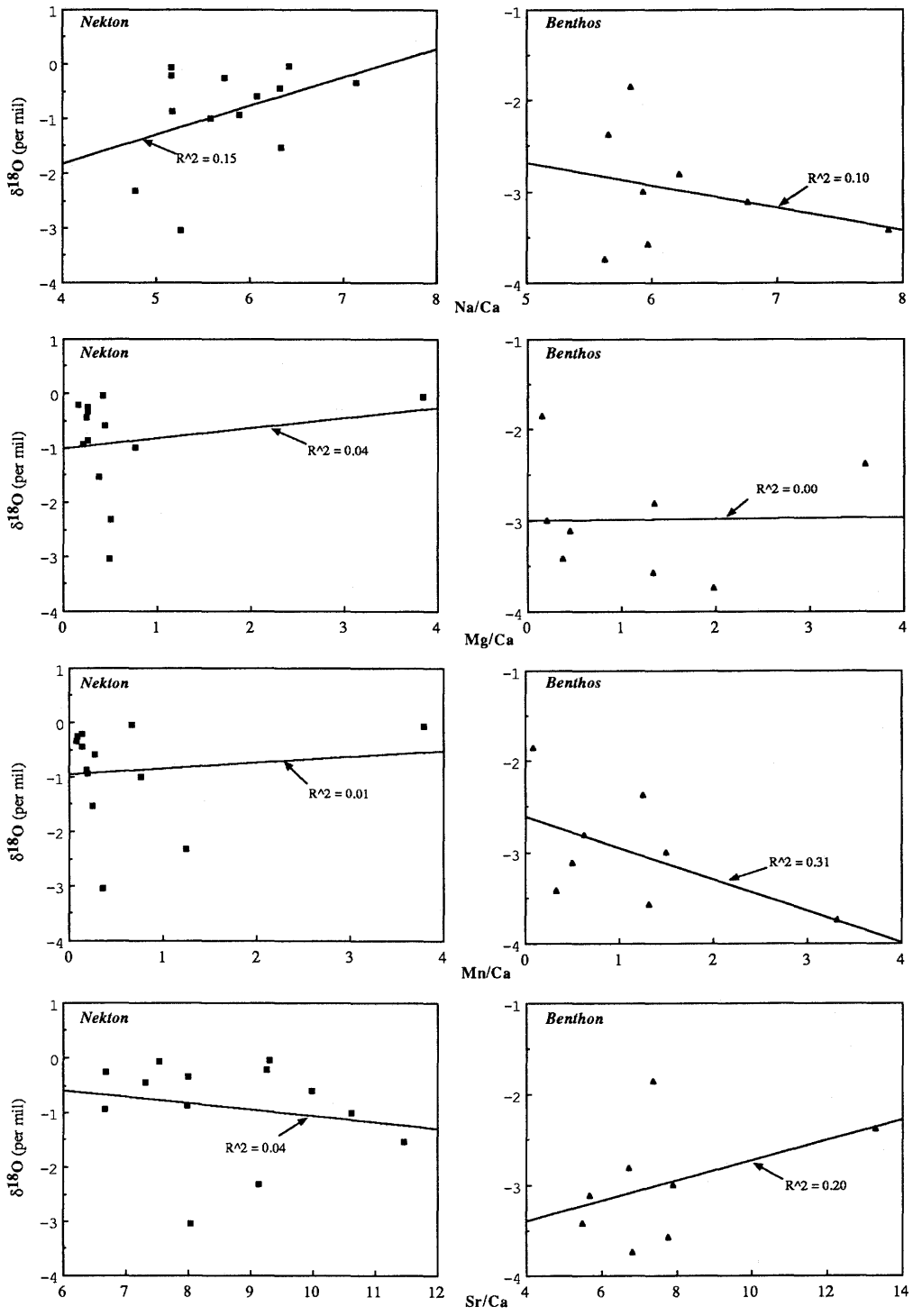


Fig. 5.2 Relation between $\delta^{18}O$ values and element/Ca ratios of the molluscan shells from the Bearpaw cyclothem. The element/Ca ratios are multiplied by a factor of 1000.

the stable-isotope compositions of the molluscan shells from the Bearpaw cyclothem that variations in the $\delta^{18}O$ values of the baculitid shells principally reflect water temperature. Processes such as sediment-seawater interaction rather than the influx of freshwater are likely responsible for the low $\delta^{18}O$ values of the benthonic inoceramids.

High Mg/Ca and Mn/Ca ratios in the aragonitic shells of baculitids from the *B. baculus* Zone could be due to diagenetic alteration although no secondary phases were detected in this specimen. However, if high Mg/Ca and Mn/Ca ratios were due to diagenetic alteration, decrease in the Na/Ca and Sr/Ca ratios, as well as $\delta^{18}O$ values, should also be expected (Whittaker *et al.*, 1987). Specimen BB(d) does not have the lowest Na/Ca and Sr/Ca ratios relative to other baculitids. An $\delta^{18}O$ value of -0.07‰, higher than those of the baculitids from other ammonite zones, eliminates the possibility that the high Mg/Ca and Mn/Ca ratios in specimen BB(d) result from diagenetic alteration of the aragonitic shell.

In addition to continental weathering products of igneous and sedimentary rocks delivered by rivers, hydrothermal processes at mid-ocean ridges, and volcanic sediments deposited in oceanic basins are the major factors affecting oceanic chemistry. Hydrothermal systems are unlikely to be the reason for the fluctuations in chemical compositions of seawater in the seaway because there is no known hydrothermal system that existed in the seaway during the Cretaceous Period (Kauffman and Caldwell, 1993). As well, volcanic sediments (ashes) cannot readily explain the anomalously high Mg/Ca and Mn/Ca ratios in the aragonitic shell of specimen BB(d) because volcanic activity was intensive during the transgressive phase, but decreased toward the end of the Bearpaw cycle. This trend is reflected in the enhanced occurrence of bentonite beds in the lower

part of the Bearpaw sequence. The lack of bentonite layers near the *B. baculus* Zone, from which specimen BB(d) was collected, suggests that high Mg/Ca and Mn/Ca ratios in aragonitic shells of BB(d) did not result from *in situ* weathering of volcanic ash falls but from sources outside of the seaway.

Continental weathering of carbonates and silicate rocks containing high Mg and Mn contents can be a major source of dissolved Mg and Mn in the seaway. Sharply increasing the rate of weathering of carbonate rocks relative to igneous rocks might elevate the Mg and Mn concentrations in the waters within the seaway during *B. baculus* time, but it should also lead to a significant increase in the Sr concentration in the seaway. As carbonates account for 75% of the strontium contribution to the oceans (Palmer and Elderfield, 1985), a change in the proportion of carbonate rocks and igneous rocks exposed in the proto-Cordillera could also have affected the Sr contents in the waters. There is no such shift in the Sr/Ca ratio in the shell of specimen BB(d), which, in contrast, has a very low Sr/Ca ratio (7.53×10^{-3}) among the baculitids analysed in this study. It is highly unlikely, therefore, that weathering of carbonate rocks produced the high Mn and Mg concentration anomalies.

The most probable cause of the high Mg and Mn anomalies in specimen BB(d) is an increase in the rate of weathering of igneous rocks containing high concentrations of both Mg and Mn in the west of the basin. In the Elkhorn Mountains of west central Montana, calc-alkaline volcanic rocks, with a thickness greater than 3000 m covered an area as large as 25,000 Km^2 in the Campanian-Maastrichtian time (Smedes, 1966; Whittaker *et al.*, 1987). Although the influx from river waters was not significant during the Bearpaw cycle, it was probably large enough periodically to deliver detritus from

newly exposed igneous rocks adjacent to the seaway, producing an increase in the Mg/Ca and Mn/Ca ratios of the seaway. The source material may not have had a high Sr concentration, which would explain why there was no accompanying significant change in the Sr/Ca ratio of the seawater as recorded in specimen BB(d).

Relatively variable element/Ca ratios (Fig. 5.2), especially Mn/Ca ratios, in the aragonitic shells of benthonic fossils suggest that benthonic influx of these elements due to sediment (volcanic ash)-water interaction likely modified the chemical composition of the bottom water in the seaway to some extent. As Figure 5.1 shows, near and before peak transgression of the Bearpaw cycle, element/Ca ratios in benthonic shells are more variable than at other times during the cycle. In fact, during transgression, volcanic activity in the west of the basin was intensive, and many bentonite beds, which are formed by *in situ* alteration of tuffs and volcanic ashes, were deposited in the basin. Interaction between these volcanic sediments and seawater may have produced pore waters with variable element/Ca ratios which migrated across the sediment-water interface because of chemical gradients and to some degree modified the chemical composition of the bottom water in the seaway. Compaction would have enhanced pore-water diffusion across the sediment-water interface, thus modifying the bottom water. Some degree of correlation between $\delta^{18}O$ values and Mg/Ca and Mn/Ca ratios in benthonic fossil shells (Fig. 5.2) indicates that this kind of modified bottom water may be one of the causes of the variable chemical compositions and low $\delta^{18}O$ values in shells of benthonic molluscs from the Bearpaw cyclothem.

Although it seems that benthonic influx of modified pore waters can, to some degree, affect the chemical composition of the bottom waters, it needs to be emphasized

that the Cretaceous seaway was a complicated system. Reduction and oxidation conditions may also mobilize elements, such as Mn, in both the sediments and seawaters. During the Late Cretaceous Epoch, both the polar and subtropical oceans, which may have had quite different chemical compositions, invaded the shallow seaway more than once, joining the internal and external forces modifying the chemical and stable isotopic compositions of the mixed waters already existing in the seaway. With transgression and regression of the seaway, the polar and subtropical oceans, together with other plausible aquatic contributions, such as influx of porewaters, met and modified each other. This resulted in the complicated, variable chemical and stable isotopic compositions of the seaway and of the shells of molluscs that lived within it, especially in the area of this study.

5.4 Rare Earth Elements (REEs)

5.4.1 REE patterns

The REE concentrations of all the molluscan shells (Table 5.3) fall within the range of modern aragonite ooze and living pteropods (Turekian *et al.*, 1973; Wang, *et al.*, 1986). The shells of nektonic baculitids are characterized by light rare earth element (LREE) enriched pattern in a shale-normalized diagram (Fig. 5.3), where La/Yb = 10 to 20. The shale-normalized REE patterns of the shells of the benthonic fossils (e.g., inoceramids) show the similar characteristic to the baculitid shells (Fig.5.4) but more variable La/Yb ratios (4 to 49). All specimens exhibit slight Ce (cerium) depletion (Fig. 5.5), except specimen BJ(a) which has slight Ce enrichment.

Table 5.3 Trace-element concentrations of the aragonitic shells of molluscan fossils from the Bearpaw cyclothem and North American shale composite (NASC).

Sample	BL(b)	BG(d)	BB(d)	BE(c)	BE(b)	BJ(a)	BR(c)	BR(a)	BCN(a)	BCN(c)	BC(b)	DC(e)	DC(a)	EJ(b)	EJ(a)	DS(c)	DS(b)	DN(c)	DN(a)	BS(d)	BS(f)	NASC
La	10.5	13.8	11.3	7.51	10.8	27.6	12.3	18.2	13.4	10.1	6.41	22.2	10.5	9.87	7.28	26.2	16.9	31.1	27.1	20.0	14.1	32.0
Ce	22.4	28.8	14.1	10.3	17.0	81.6	15.6	38.5	30.7	19.1	11.1	44.1	21.8	14.6	11.4	45.5	33.6	69.5	56.7	46.1	31.8	73.0
Pr	2.80	3.58	1.61	1.25	1.83	10.2	1.50	4.39	3.77	2.28	1.31	5.86	2.67	1.60	1.42	6.07	4.12	8.27	6.66	5.73	3.77	7.90
Nd	11.0	13.8	6.35	5.16	7.81	42.6	5.94	17.2	14.8	8.95	5.11	23.9	10.8	7.01	5.62	25.0	16.0	32.3	25.4	22.8	14.3	33.0
Sm	1.28	1.40	0.60	0.87	1.31	4.04	0.71	2.10	1.32	0.89	0.79	2.64	1.27	1.36	0.60	2.75	2.01	3.25	2.09	2.31	1.25	5.70
Eu	0.22	0.22	0.12	0.18	0.24	0.60	0.17	0.36	0.22	0.13	0.17	0.58	0.22	0.23	0.09	0.45	0.31	0.53	0.31	0.42	0.25	1.24
Gd	0.79	0.79	0.40	0.89	0.85	1.71	0.61	1.38	0.86	0.53	0.49	1.55	0.79	1.00	0.44	1.50	1.01	1.65	1.16	1.25	0.67	5.20
Tb	0.07	0.06	0.04	0.07	0.08	0.09	0.05	0.10	0.05	0.04	0.06	0.12	0.07	0.10	0.04	0.13	0.11	0.13	0.07	0.11	0.03	0.85
Dy	0.39	0.29	0.19	0.41	0.38	0.56	0.30	0.38	0.31	0.23	0.21	0.53	0.42	0.43	0.27	0.66	0.58	0.69	0.30	0.56	0.21	5.80
Ho	0.07	0.05	0.03	0.06	0.07	0.08	0.06	0.06	0.05	0.03	0.03	0.10	0.08	0.05	0.06	0.11	0.11	0.11	0.06	0.09	0.03	1.04
Er	0.21	0.16	0.08	0.15	0.14	0.20	0.16	0.16	0.11	0.08	0.07	0.21	0.17	0.14	0.16	0.24	0.25	0.26	0.11	0.23	0.05	3.40
Tm	0.03	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.11	0.01	0.01	0.03	0.02	0.01	0.02	0.03	0.03	0.03	0.01	0.03	0.01	0.50
Yb	0.14	0.09	0.05	0.11	0.12	0.08	0.08	0.12	0.08	0.06	0.02	0.18	0.16	0.07	0.16	0.17	0.20	0.18	0.07	0.15	0.02	3.10
Lu	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.48
ΣREE	50	63	35	27	41	170	38	83	66	42	26	102	49	36	28	109	75	148	120	100	66	173
La/Yb	7	14	18	6	8	29	13	14	14	16	20	12	7	16	4	16	9	16	42	12	44	
Th	0.03	0.04	0.05	0.03	0.12	0.54	0.01	0.43	0.06	0.15	0.41	0.07	0.03	0.12	0.19	0.16	0.16	0.19	0.04	0.01	0.03	
U	0.69	0.58	0.48	0.24	0.47	0.52	2.00	1.78	0.31	0.59	0.14	0.37	0.29	1.69	0.89	0.68	0.96	0.90	0.66	1.62	0.65	
V	4.04	0.91	1.68	0.85	1.99	0.99	0.47	0.77	1.55	2.78	0.42	1.11	0.32	2.18	1.36	1.42	1.44	1.46	1.11	1.66	0.42	
Cr	0.70	0.59	1.49	0.97	2.00	0.34	0.87	2.28	1.85	1.32	1.44	0.81	0.84	0.94	0.46	0.86	1.55	0.68	0.97	0.82	0.67	
Mo	0.72	0.29	0.45	2.89	0.72	9.31	0.11	1.30	0.30	0.04	1.33	0.23	0.19	0.40	1.53	0.18	0.82	0.20	0.70	0.27	0.06	
Th/U	0.04	0.07	0.10	0.13	0.26	1.04	0.01	0.24	0.19	0.25	2.93	0.19	0.10	0.07	0.21	0.24	0.17	0.21	0.06	0.01	0.05	
Th/V	0.01	0.04	0.03	0.04	0.06	0.55	0.02	0.56	0.04	0.05	0.98	0.06	0.09	0.06	0.14	0.11	0.11	0.13	0.04	0.01	0.07	
Th/Cr	0.04	0.07	0.03	0.03	0.06	1.59	0.01	0.19	0.03	0.11	0.29	0.09	0.04	0.13	0.41	0.19	0.10	0.28	0.04	0.01	0.05	
Th/Mo	0.04	0.14	0.11	0.01	0.17	0.06	0.09	0.33	0.20	3.75	0.31	0.30	0.16	0.30	0.12	0.89	0.20	0.95	0.06	0.04	0.50	

Note: Concentrations in ppm; North AMerican shale composite (NASC) is from Taylor and McLennan (1985)

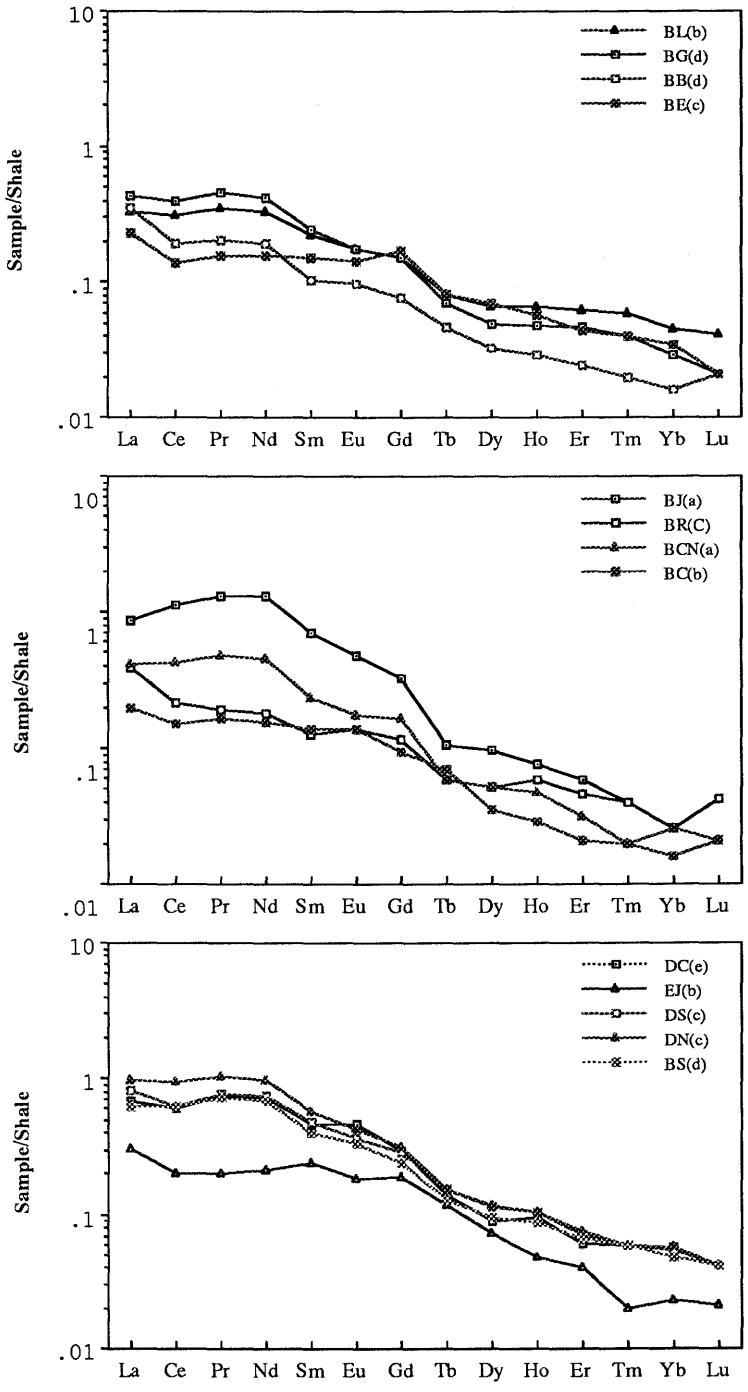


Fig. 5.3 Shale-normalized REEs in aragonitic shells of nektonic baculitid shells from the ammonite zones of the Bearpaw cyclothem. North America shale composite (NASC) for normalization is from Taylor and McLennan (1985).

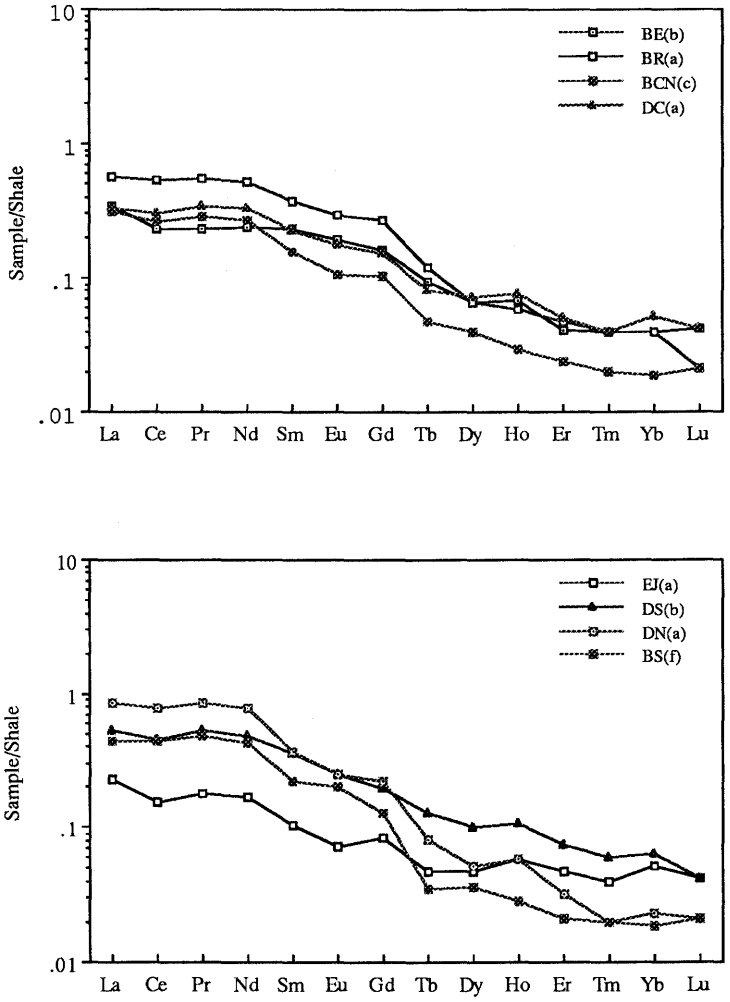


Fig. 5.4 Shale-normalized REEs in aragonitic shells of benthonic fossils from the ammonite zones of the Bearpaw cyclothem. North American shale composite (NASC) for normalization is from Taylor and McLennan (1985).

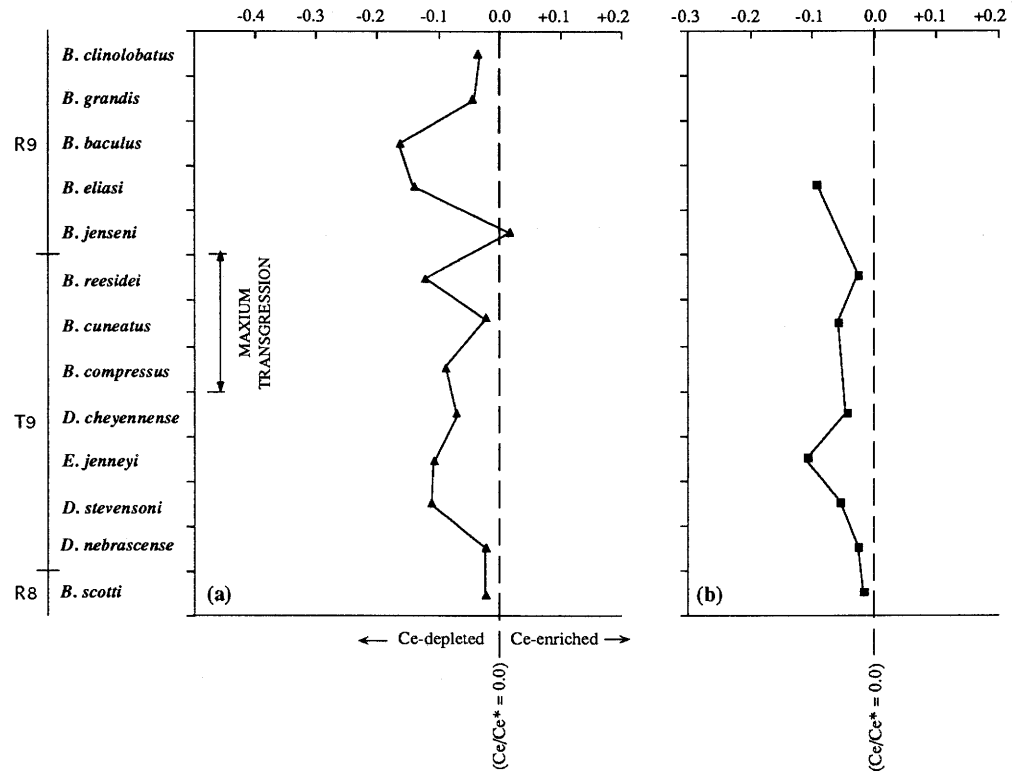


Fig. 5.5 Biostratigraphic profiles of Ce-anomaly (Ce/Ce*) in aragonitic shells of (a) nektonic, and (b) benthonic fossils from the Bearpaw cyclothem. The Ce anomaly results from the oxidation and reduction of Ce. $Ce/Ce^* = \log[2Ce_N/(La_N + Pr_N)]$. Abbreviations: *B.* = *Baculites*,*D.* = *Didymoceras*, *E.* = *Exiteloceras*. T9 and R9 represent the transgressive and regressive phases of the Bearpaw cyclothem respectively; R8 represents regressive phase of the Claggett cyclothem (Gill and Cobban, 1966, 1973; Kauffman and Caldwell, 1993). Maximum transgression of the Bearpaw cycle is determined from ammonite zones (Gill and Cobban, 1973; Caldwell, 1968).

5.4.2 REEs of molluscan shells -- A recorder of paleoenvironments

REEs of the shells of organisms have been used as tools to explore the chemistry of ancient oceans and seas (e.g., Boyle, 1981; Palmer and Elderfield, 1985; Wang *et al.*, 1986; Whittaker and Kyser, 1993). The accuracy with which carbonate shells record the REE compositions of ancient oceans and seas has, however, been the subject of considerable debate (Wang *et al.*, 1986; Whittaker and Kyser, 1993) primarily because concentrations of REEs in most biocarbonates are greater than those expected from the inorganic precipitation of carbonates with REE/Ca ratios similar to modern seawater (Shaw and Wasserburg, 1985).

REEs in carbonates are located in the $CaCO_3$ structure, in the Fe-Mn-oxyhydroxide coating, and adsorbed onto the $CaCO_3$ mineral surface. The Fe-Mn-O coatings form on the surface of modern foraminifera during diagenesis. Boyle (1981, 1983) indicated that this authigenic phase is a source of contamination in trace element analysis. Palmer (1985) reported that the Fe-Mn-O coating is responsible for about 90% of the REEs measured and that, in contrast, the concentration of REEs in the $CaCO_3$ structure is very low. Palmer found that Fe contents correlate with REE concentrations in foraminifer tests with an FeMn-rich coating, but that there was no correlation between Fe and REEs in the carbonate structure of the tests, suggesting that the REE contents of foraminifera are dominated by coating phases, not by the calcite tests.

Palmer and Elderfield (1986) and Whittaker and Kyser (1993) postulated that the Fe-Mn-O coatings likely occur on all fossils, including molluscan shells such as those used in the study. Potentially, this post-mortem coating could have contaminated or affected REEs of these molluscs. The ratio of surface area to volume of shell materials

in molluscs is significantly lower than in foraminifera, however, so that the REEs of the molluscan shells should not be affected as much by the Fe-Mn-O coating on the surface. In practice, there is a lack of correlation ($r^2 = 0.005$) between REE and Mn contents in aragonitic shells used in this study, indicating that the Fe-Mn-O coating is probably not related to the REEs of molluscan shells (Fig.5.6). As a precaution, the outermost layers of the aragonitic shells were removed prior to analysis, as suggested by Whittaker and Kyser (1993), further reducing the influence of the diagenetic coating on the concentrations of REEs in the molluscan shells used.

Turekian *et al.* (1973) found that living pteropod shells have high concentrations of REEs which they attributed to the incorporation of submicroscopic, REE-rich, Fe-hydroxide or Fe-phosphate flocs in the shells. Shaw and Wasserburg (1985) argued that Fe-phosphate flocs may be present in the molluscan shell matrix. However, given their scarcity, they should not be the major factor affecting the REE concentrations in aragonitic shells of the mollusc studied. Whittaker and Kyser (1993) reported that the aragonite and calcite shells of molluscs from the Western Interior Basin had similar concentrations of REEs, but shale-normalized REE patterns are substantially different for these two phases, suggesting that Fe-flocs do not exert a major control over the REEs in molluscan shells.

As mentioned previously, molluscan organisms deposit their shells from the extrapallial fluids between the outside mantle epithelium and the inner shell surface. These fluids contain many organic materials (e.g., amino acids, proteins, organic acids, and lipids) secreted by the cells of the mantle, and they are important in controlling biomineralization. The organic materials envelop and commonly permeate every mineral

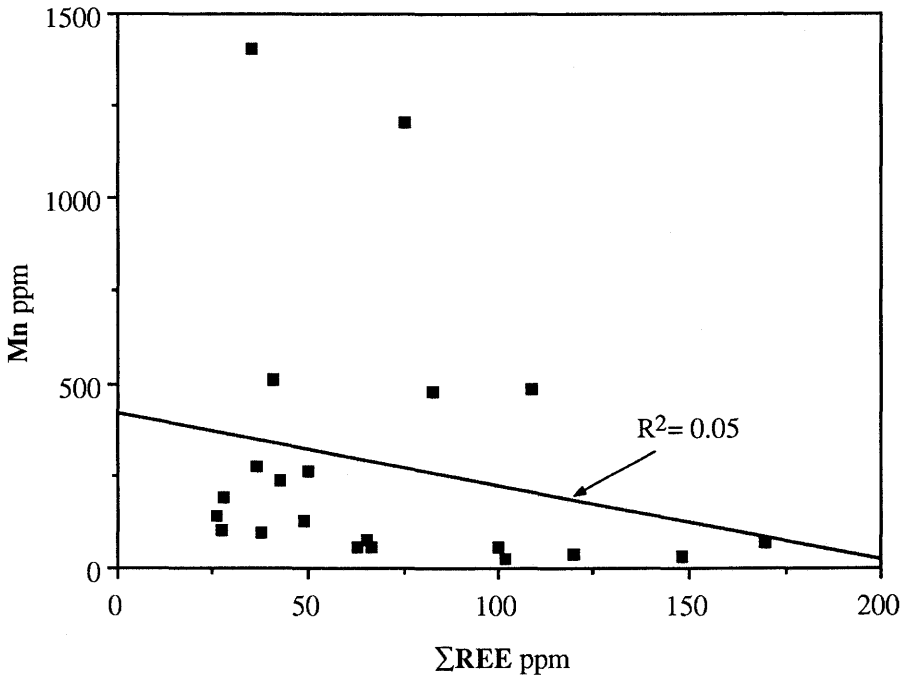


Fig. 5.6 Relation between Mn and total REE concentrations in molluscan shells from the Bearpaw Formation and its equivalents of the Western Interior Basin. A lack of correlation betwen Mn and REEs suggests that the REEs in the shells are not associated with the Fe-Mn-rich coating formed during diagenesis.

unit in carbonate shells. Studies have indicated that nucleation, orientation, and even crystal type of the biocarbonates are controlled by these organic materials (Tucker and Wright, 1990). Organic materials potentially provide absorptive surfaces for REE scavenging. The thin organic coatings on the surfaces of calcite and aragonite mineral units in molluscan shells might have an important influence on the relative absorptive behaviour of individual REEs onto substrate surfaces during growth of the molluscan organisms (Whittaker and Kyser, 1993). As different organic matrices within molluscan shells may have different chemical activities, the differences between absorptive characteristics of organic matrices in carbonate shells may be the reason for variations in the REE concentration and distribution in the carbonate shells of different organisms (Whittaker and Kyser, 1993). They further suggested the possibility that the differences in the relative REE concentrations of biogenic calcite and aragonite of molluscan shells may result from partition of the REEs during carbonate growth due to vital effects.

In this study, efforts were made to evaluate the effects of the REEs in the Fe-Mn-O coatings and organic matrices on the REE concentrations of the molluscan shells used. The approach was very simple: choose several molluscan shell samples, remove the Fe-Mn-O coatings and organic matrices within the shells, then compare the concentrations of the trace-elements in treated shells with those of original shells. The Fe-Mn-O coatings were removed by physically cleaning shell samples followed by soaking the crushed samples in a warm reducing solution (see APPENDIX I for the detailed methods). After cleaning the Fe-Mn-O coatings or organic materials, the trace elements of the treated samples, as well as those of untreated samples, were analysed using ICP-MS (Table 5.4). Differences between the REE concentrations of untreated samples and

Table 5.4 Comparision between the trace-element concentrations of treated samples and those of untreated samples

Sample	BS(c)	BS(c)[1]	DC(a)	DC(a)[1]	BJ(a)	BJ(a)[2]
Y	7.89	6.98	4.49	4.82	5.32	5.80
La	10.76	10.78	10.56	10.09	26.52	25.32
Ce	18.94	18.65	19.05	18.54	69.79	70.11
Pr	2.48	2.39	2.37	2.26	9.10	9.32
Nd	9.80	9.66	9.15	9.17	36.77	39.44
Sm	1.04	0.90	0.98	0.91	3.56	3.76
Eu	0.16	0.17	0.17	0.16	0.48	0.53
Gd	0.62	0.62	0.68	0.68	1.36	1.41
Tb	0.07	0.07	0.07	0.07	0.11	0.11
Dy	0.39	0.34	0.42	0.37	0.50	0.46
Ho	0.07	0.07	0.07	0.07	0.08	0.09
Er	0.16	0.19	0.20	0.16	0.19	0.16
Tm	0.02	0.02	0.02	0.03	0.02	0.03
Yb	0.14	0.14	0.12	0.11	0.14	0.13
Lu	0.02	0.02	0.02	0.02	0.01	0.01
Th	0.03	0.03	0.05	0.04	0.11	0.11
U	0.75	0.34	0.19	0.17	0.22	0.20
V	2.86	2.74	0.45	0.42	1.39	1.23
Cr	1.10	1.21	0.78	0.86	4.48	11.09
Mo	0.15	0.16	0.14	0.15	0.44	1.13

Notes: "1" means organic matter in the sample has been removed
"b" means both organic matter and FeMn-coating have been removed
Techniques used are described in APPENDIX I.

those of treated samples are minimal, indicating that either organic matrices or the Fe-Mn-O coatings do not significantly affect the REEs within the molluscan shells. The difference in the REE patterns of calcite and aragonite should be mainly due to their different crystal structures. LREEs have larger radii than heavy rare earth elements (HREEs) and are more easily contained in the open aragonite structure, whereas HREEs are preferentially contained in the denser structure of calcite. Therefore, the characteristics and patterns of the REEs in molluscan shells should mirror those of the seawaters and reflect variations in paleoenvironmental conditions.

5.4.3 Implications of Ce-anomalies

The REEs comprise an extremely coherent group. The fourteen REEs in nature commonly exist in the soluble 3+ oxidation state and exhibit very similar chemical properties. Cerium (Ce) and europium (Eu), however, are unique in having multiple oxidation states. The oxidation of Ce (III) to Ce (IV) or reduction of Eu (III) to Eu (II) leads to anomalies of Ce and Eu relative to the remaining twelve REEs, which are strictly trivalent under oxidizing and reducing conditions.

The *in situ* investigation of REE distribution in the anoxic waters of the modern Cariaco Trench (De Baar *et al.*, 1988) shows that Eu does not change its oxidation state or fractionate from other REEs. Many recent studies also indicate that Eu exhibits similar geochemical behaviour in the waters of other modern anoxic and suboxic oceans or seas (German and Elderfield, 1989, 1990; German *et al,* 1991). Moreover, thermodynamic considerations rule out the possibility of low-temperature reduction of Eu (III) to Eu (II) (Sverjensky, 1984). Relative to the other REEs, significant

fractionation of Eu may take place during high-temperature hydrothermal alteration processes, as in the mid-oceanic ridge system, because of the expected stability of divalent Eu during these processes (Michard *et al.*, 1983; Sverjensky, 1984). This suggests that Eu does not reflect oxidation and reduction conditions in low-temperature environments.

Unlike Eu, Ce concentrations in seawater are dominated by the oxidative-precipitation and reductive-dissolution cycle under low-temperature conditions. Changes in Ce are conveniently related to the adjacent elements, lanthanum (La) and praseodymium (Pr) by:

$$Ce/Ce^* = \log [2Ce_N/(La_N + Pr_N)] \qquad (5.1)$$

Where N indicates normalization to North American shale composite (NASC) and Ce/Ce* represents a quantitative determination of the variation of Ce relative to its neighbouring REEs. Positive values of Ce/Ce* indicate that Ce is enriched compared to La and Pr, whereas negative values of Ce/Ce* mean that Ce is depleted. Under anoxic and dysoxic conditions, Ce (III) is stable and remains soluble in seawater, thus Ce/Ce* values are close to zero. In the presence of oxygen, Ce(III) will be oxidized to insoluble Ce (IV) oxides and gradually fractionated from other REEs, producing a negative Ce anomaly in shale-normalized REE patterns.

Most of the molluscan shells analysed exhibit slight depletion of Ce relative to the rest of the REE series (Fig.5.4). Baculitid specimen BJ(a) from the *B. jenseni* Zone has a slight Ce enrichment with a Ce/Ce* value of 0.02. The relatively high values of

Ce/Ce* (absence of obvious negative anomaly) in all the benthonic and nektonic fossils indicate that there was little or no fractionation of Ce from other REEs in the Bearpaw sea. This absence of negative Ce anomalies closely resembles the REE patterns in dysoxic and anoxic waters of modern oceans and seas (German and Elderfield, 1989, 1990; German *et al.*, 1991; Sholkovitz *et al.*, 1992; De Baar *et al.*, 1985, 1988). In well-oxygenated environments of the modern open oceans and seas, the water generally has very obvious Ce depletions, with the Ce/Ce* lower than -0.22 (German *et al.*, 1991). Although some of the baculitids studied do have very low Ce/Ce* values (e.g BB(d)) with a Ce/Ce* value of -0.16), they are still considerably higher than -0.22.

The lack of obvious Ce depletion in the aragonitic shells of the molluscan fossils analysed suggests that the seaway was not well-oxygenated in either its surface or bottom waters throughout most of the Bearpaw cycle. If the Bearpaw sea had been dynamic and well-oxygenated, Ce of the waters would have been strongly depleted, much as it is in modern open oceans and seas, resulting in the molluscan fossils having very low Ce/Ce* values (below -0.22).

The oxygen-deficient environment and limited vertical mixing within the seaway is well reflected by the general characteristics of the sedimentary rocks and faunas of the Bearpaw Formation and its equivalents. These rocks consist mainly of silty clays and sands, generally showing some degree of lamination. Although not strongly affected in general, many have been disturbed by organic activity as they exhibit some degree of bioturbation (Caldwell 1968, 1982). Many of the bentonite seams have somewhat ragged tops, as if the volcanic ash was only weakly disturbed by bottom currents as mud deposition was resumed. Another important piece of evidence for a subnormal oxygen

level in the seaway waters is the character of the Bearpaw fauna. Through most of the Late Cretaceous Epoch, the seaway was characterized by a low-diversity fauna dominated by ammonites and bivalves, quite unlike the much more varied fauna that prevailed under contemporary well-oxygenated conditions (Kauffman and Caldwell, 1993).

According to the Rhoads-Morse-Byers (RMB) model (Rhoads and Morse, 1971; Rhoads *et al.*, 1991), the Bearpaw sea seems to be a dysoxic environment with dissolved oxygen levels between 0.1 and 1.0 ml/l. In oxic conditions with dissolved oxygen levels above 1.0 ml/l, both bottom and surface waters are well oxygenated, supporting a diverse and prolific fauna, and sediments are strongly bioturbated, destroying all or most of their fine sedimentary structures. With declining levels of dissolved oxygen, there is a progressive loss of organic species, especially of benthonic species with carbonate shells, until all of these disappear at variably low levels of dissolved oxygen below 1.0 ml/l (Wignall, 1994), but most commonly at levels of 0.3 to 0.5 ml/l (Tyson and Pearson, 1991). Bioturbation declines with decreased organic activity, and there is increased preservation of fine-scale sedimentary structures, such as lamination. Certain organisms, some bivalves for example, can survive in dysoxic conditions and survive well if the decline in oxygen level is gradual and they have an opportunity to become acclimatized (Wignall, 1994).

Although declining in diversity, foraminifera, like benthonic bivalves, can also live in declining oxygen-level conditions. Benthonic foraminiferal assemblages have been reported from oxygen-depleted environments in, for example, the Devonian (Gutschick and Wuellner, 1983), the Jurassic (Bernhard, 1986), the Cretaceous rocks of England

(Hart and Bigg, 1981), and the Miocene and Pliocene of the Mediterranean (Thomas, 1980; Katz and Thunell, 1984). Foraminifera appear less affected by oxygen levels than other benthos in modern environments (Wignall, 1994), and consequently they can even be found in the sediments of upper anaerobic environments. Douglas (1981) postulated that an abundance of foraminifera in low-oxygen environments may be due to an absence of usual predators. Due to the difficulty of calcium-carbonate secretion in low-oxygen conditions, however, foraminifera tend to be thin-shelled and poorly ornamented (Douglas, 1981; Bernhard 1986). For this reason agglutinating foraminifera are proportionately more common in oxygen- deficient environments than in well-oxygenated environments. The Bearpaw Formation and its equivalents contain foraminifera fauna which are rich in number and variety, and they exhibit the general characteristics of those prevailing in oxygen-deficient environments (North and Caldwell, 1970, 1975; Caldwell *et al.*, 1993). Generally speaking, in the important South Saskatchewan River valley section (Caldwell, 1968; North and Caldwell, 1970), agglutinated-walled species are dominant both in number and variety in the lower part of the section (Sherrard, Demaine, Beechy, and Ardkenneth members) and in the upper part of the section (Cruikshank and Aquadell members). Even in the intervening Snakebite Member, denoting the period of peak transgression, agglutinated-walled foraminifera are still common.

Variations in the stable-isotope compositions of the coeval benthonic and nektonic molluscan fossils from the Bearpaw cyclothem, insofar as they point to isotopic stratification of the waters, infer low-dynamic and low-oxygen levels of the Bearpaw sea. Long-term stratification of the sea in itself hints at weak dynamic conditions. Had the

seaway been highly dynamic, the sea would have been well mixed in both the upper and bottom waters, so that the shallow waters -- perhaps no more than 100 m deep (Gill and Cobban, 1966; Caldwell, 1968) -- would have been well mixed, and differences between stable-isotope compositions of the bottom and surface waters would have been very slight.

Whittaker and Kyser (1993) investigated REEs in molluscan shells from the Cretaceous Interior seaway of Late Cenomanian to Maastrichtian age. Like the shells analysed in this study, they found their fossils to have high Ce/Ce* values (between -0.17 to 0.13), with most near zero, indicating no Ce depletion in the seawater. This suggests that the seaway waters were probably not well-oxygenated through most of the Late Cretaceous time, not just during the Bearpaw cycle. Whittaker and Kyser (1993) did not attribute high Ce/Ce* ratios to oxygen-deficient conditions of the seaway, however, as the global anoxic event (the Bonarelli OAE) spanning the Cenomanian-Turonian transition is not recorded as a positive Ce anomaly in the specimens analysed. Additionally, organic carbon contents are variable and relatively low in many of the rocks from which molluscan fossils, without obvious Ce depletion, were collected.

Traditionally, high concentrations of organic carbon have been considered to be a characteristic of low-oxygen environments: the prevailing explanation is that anoxic bottom waters enhance the preservation of organic carbon and hence generate the high concentrations of it. Pedersen and Calvert (1990) have suggested, however, that it is high primary production of organic carbon, not water-column oxygen-deficiency, that provides the first-order control on accumulation of organic-rich facies in modern oceans, and that anaerobic or dysaerobic conditions are a consequence of this high productivity.

The preservation of organic matter in marine sediments depends on the degree to which sediment-dwelling bacteria are able to metabolize constituent components of the deposited organic materials, not upon pre-existing oxygen deficiency of the seawater. A considerable volume of evidence supports this position. Experiments and observations showed that the rate of decomposition of algae was roughly the same under oxic and anoxic conditions in either estuarine or truly marine waters (Foree and McCarty, 1970; Jewel and McCarty, 1971; Jorgensen, 1982). Kristensen and Blackburn (1987) found that the degradation rate of organic matter in natural, shallow-water sediments, incubated under anoxic conditions, was actually higher than that under oxic conditions. Henrich and Reeburgh (1987) also pointed out that rates of organic-matter mineralization are similar under oxic and anoxic conditions. In the modern Black Sea, the typical euxinic basin, the sediments are not particularly enriched in organic matter despite the presence of an anoxic water column, and a pre-modern sapropel containing an extremely high concentration of organic carbon was shown to have been deposited during the Holocene Epoch at a time when the basin was oxic (Calvert, 1990). Like the Black Sea, the organic-carbon content in fine-grained bottom sediments of anoxic fjords in Norway is generally less than 6% by weight, differing little from its content in sediments of similar texture that accumulated in oxic inlets or fjords (Calvert, 1987; Pedersen and Calvert, 1990). From all of this, Pedersen and Calvert (1990) concluded that, over a time-scale of hundreds of years, there likely will be no significant difference in the amount of organic carbon preserved in oxic and anoxic environments.

In terms of reconstructing the Late Campanian-Early Maastrichtian environment of the Western Interior Seaway, the total organic matter present throughout the Bearpaw

Formation and its equivalents has not yet been determined. There is no indirect evidence that it was abnormally high, even during parts of the transgressive and regressive phases of the marine cycle (as has been shown to be the case for some earlier Late Cretaceous cycles). Pedersen and Calvert's (1990) recognition that the accumulation of organic matter is largely controlled by organic productivity in surface waters, which is a function of nutrient supply and solar radiation, seems entirely reasonable, but if preservation of this organic matter does not automatically require anoxia or dysoxia of the bottom waters, then abnormally high proportions of organic matter, even if present in the Bearpaw Formation and its equivalents, could not be taken as a clear signal of anoxia or dysoxia anyway. It would seem reasonable to suggest only that, as indicated by lack of obvious Ce depletion in the molluscan shells analysed, the Bearpaw sea was somewhat dysoxic, and that lack of any obvious organic-rich rocks in the succession point to organic productivity in the surface waters of the Bearpaw sea probably being low.

5.5 Other Trace Elements

Some trace elements (Cr, V, U and Mo) have been proposed as tracers of redox conditions of marine sedimentary environments because their concentrations are affected by variations in the redox conditions of the oceans (Wright *et al.*, 1984; Calvert and Pedersen, 1993). Molybdenum (Mo) and uranium (U) behave conservatively in the ocean, their concentrations being more or less constant between different oceans and water depths (Calvert and Pedersen, 1993). This is believed to be due to the relatively unreactive nature of their dissolved species, namely molybdate (MoO_4^{2-}) and the uranyl carbonate complex [$UO_2(CO_3)_3^{4-}$], in oxygenated seawater. In spite of this lack of

chemical reactivity under oxic conditions, these metals are removed from seawater under anoxic conditions. Chromium (Cr) and Vanadium (V) occur in oceans and seas in at least two oxidation states, and they are more reactive than Mo and U because their concentrations vary with depth in the ocean. Like U and Mo, they should be removed from the ocean and incorporated into anoxic sediments due to the propensity of reduced species of both these elements to precipitate as soluble oxides or hydroxides, or to be strongly adsorbed onto particle surfaces (Emerson and Huested, 1991). In contrast, Thorium (Th) is relatively immobile in aqueous solution, so that variations in Th/Cr, Th/V, Th/U and Th/Mo ratios should be the function of the redox conditions of the oceans. These ratios should be much lower under anoxic conditions and higher under oxic conditions (Wright *et al.*, 1984).

Variations in Th/Cr, Th/V, Th/U, and Th/Mo ratios of molluscan shells with the biostratigraphic sequence should reflect changes in the redox conditions of the Bearpaw sea with time, and these ratios should vary correspondingly with Ce/Ce* values. However, Th/Cr, Th/V, Th/U and Th/Mo ratios in the molluscan shells in this study do not show any sympathetic variations with Ce/Ce* values through biostratigraphic sequence (Fig. 5.7). The generally low correlation among these ratios and Ce/Ce* (Fig. 5.8, Fig. 5.9) suggests that factors other than reduction and oxidation in the seaway had a greater influence on these parameters. Unlike Ce, which can be compared to its neighbouring REEs to trace redox conditions, there is no quantitative parameter like Ce/Ce* which can single out these elements from other processes affecting their concentrations in seawaters. This probably is a factor limiting the utility of these elements in fossil shells for inferring redox conditions of ancient oceans and seas.

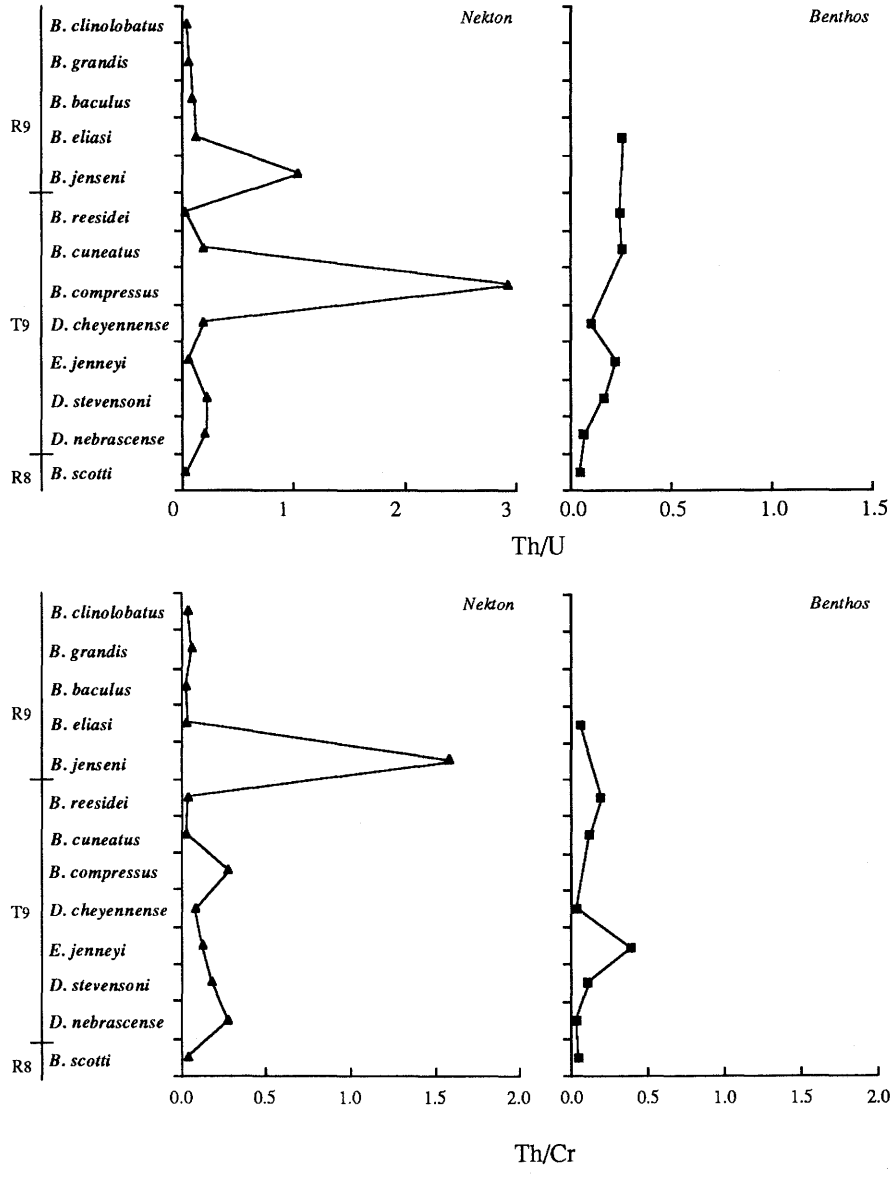


Fig. 5.7 Variations in Th/U and Th/Cr ratios within aragonitic shells of molluscan fossils from the ammonite zones of the Bearpaw cyclothem. Abbreviation: *B.* = *Baculites*, *D.* = *Didymoceras*, *E.* = *Exiteloceras*. T9 and R9 represent the transgressive and regressive phases of the Bearpaw cyclothem, respectively; R8 represents the regressive phase of the Claggett cyclothem.

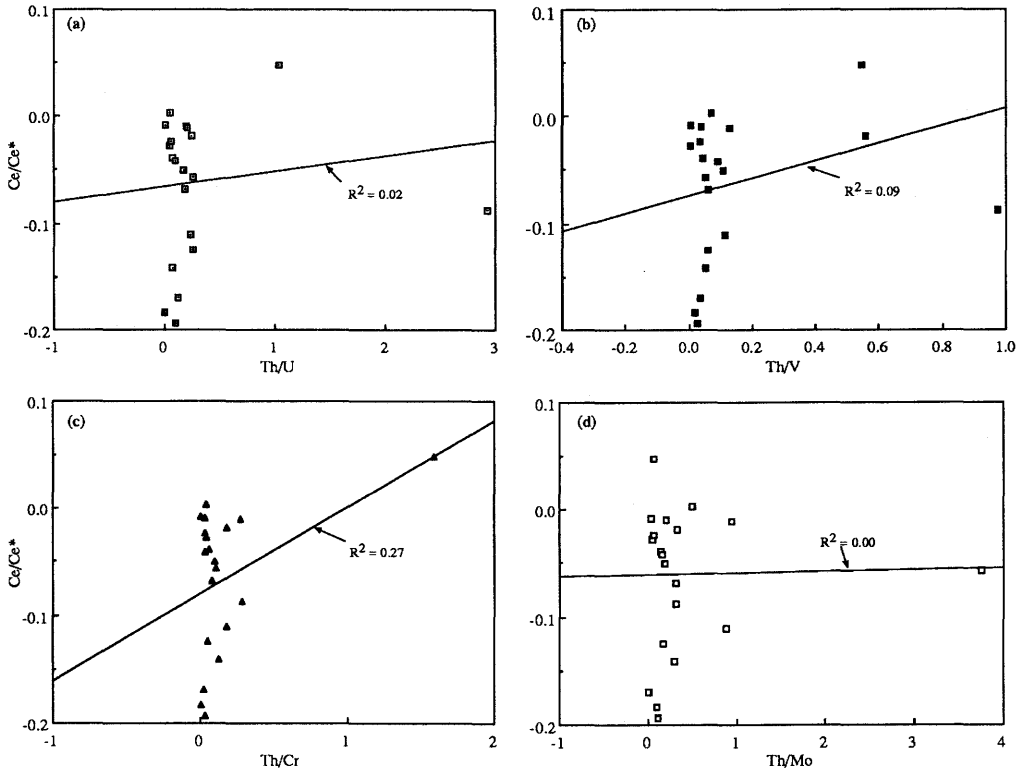


Fig. 5.8 Relation between Ce/Ce* and (a) Th/U, (b) Th/V, (c) Th/Cr and (d) Th/ Mo ratios in aragonitic shells of molluscan fossils from the Bearpaw cyclothem. Low coefficients indicate that the mechanisms other than redox conditions controlled the distribution of these elements in the seaway.

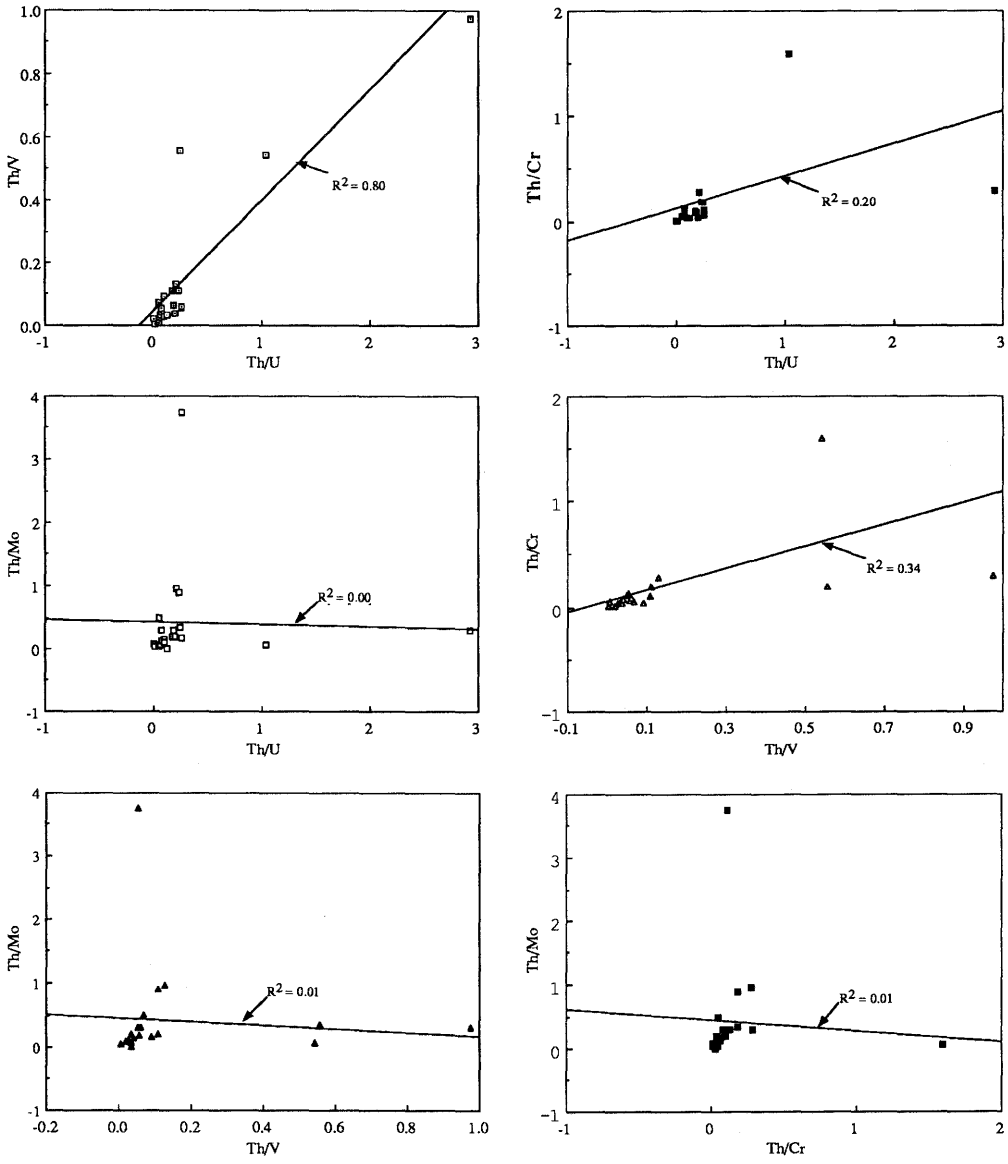


Fig 5.9 Relation among Th/U, Th/V, Th/Cr and Th/Mo ratios in aragonitic shells of molluscan fossils from the Bearpaw cyclothem.

5.5 SUMMARY

As with the stable-isotope data, constant element/Ca ratios in nektonic baculitids indicate that influx of run-off into the seaway was insignificant and more or less constant, implying that the Bearpaw sea was not brackish. Variable element/Ca ratios in benthonic fossils and some degree of correlation between these ratios and $\delta^{18}O$ values suggest that the chemistry of the bottom waters in the seaway may have been affected by benthic influx of these elements at the sediment-water interface.

REE data can provide useful information on environmental (redox) conditions in the seaway. Carbonate shells of molluscan fossils exhibit slight Ce-anomalies, with Ce/Ce* values of -0.16 to 0.02, indicating little or no fractionation of Ce from the rest of the REEs. No obvious Ce anomalies in either the benthonic or nektonic fossils implies a degree of oxygen deficiency in both the upper and bottom waters of the seaway through most of the Bearpaw cycle. Oxygen-deficient conditions may then account, at least partially, for the character of the Bearpaw fauna. Redox conditions of the seaway during the Late Cretaceous Epoch need further study, supported by evidence from detailed investigation of fine sedimentary structures and various kinds of fossils, especially trace fossils.

6. SYNOPSIS OF PRINCIPAL CONCLUSIONS

Stable isotopic and chemical compositions of molluscan shells from the Bearpaw cyclothem in the middle part of the Western Interior Basin provide a record of the prevailing paleoenvironment during the Late Campanian and Early Maastrichtian portion of the Late Cretaceous Epoch. $\delta^{18}O$ values obtained from baculitid ammonites vary through the biostratigraphic sequence, the pattern of which is readily explained by fluctuations in temperature of the near-surface waters of the Bearpaw sea rather than fluctuations in fresh-water influx. The $\delta^{18}O$ values of these fossils indicate increasing temperature of the near-surface waters during the Bearpaw transgression, and decreasing temperatures during regression. This may correlate to a pulse of tectonic activity and volcanism west of the basin in the proto-Cordillera, which caused a rise and fall in the CO_2 content in the atmosphere.

Influx of freshwater to the Bearpaw sea was low, and the sea was not brackish. This suggests low precipitation and run-off from rivers on the western flank of the basin, where drier than normal climatic conditions prevailed. Low freshwater influx is further supported by relatively constant element/Ca ratios of the baculitids and absence of correlation between the $\delta^{18}O$ values and these ratios. Compared to the older Greenhorn (Cenomanian-Turonian) and Niobrara (Turonian-Santonian) cyclothems, the $\delta^{18}O$ values of the ammonite shells from the Bearpaw cyclothem are much closer to those of shelled animals that lived in coeval open oceans and seas. The more open-marine

conditions implied find support in the overall character of the Bearpaw fauna and in the contemporary vegetation of adjacent land areas within the Western Interior.

Large differences in stable isotopic compositions are present among the coexisting molluscs from the Bearpaw cyclothem. The baculitids generally have the highest average $\delta^{18}O$ values and lowest average $\delta^{13}C$ values, whereas the inoceramids exhibit the opposite trend. This implies that these different mollusc lived in isotopically distinct, stratified reservoirs within the Bearpaw sea. As inoceramids were unquestionably benthonic, the baculitids probably lived in the upper part of the water column. However, not all ammonites were nektoplanktonic, living in the upper water column; stable isotopic compositions of the scaphitid ammonites suggest that they lived in different parts of the water column, and those of the heteromorphic didymoceratids suggest that they were bottom dwellers, rather like the inoceramid bivalves.

Modification of the bottom waters of the Bearpaw sea by sediment-water interactions have been partly responsible for the inferred isotopic stratification, as these interactions may also have been responsible for modifying other aspects of the chemical composition. The more variable ratios of various elements to Ca as opposed to baculitids suggest this possible modification of the bottom waters.

The molluscan fossils from the Bearpaw cyclothem have values of Ce/Ce* near zero, indicating little or no fractionation of Ce in the Bearpaw seawater, as is true of dysoxic and anoxic zones in modern oceans and seas. Hence the Bearpaw sea was probably neither well-oxygenated nor very dynamic. Sedimentary structures and the fauna of the Bearpaw and equivalents are consistent with a measure of dysoxia. As the molluscan shells from older rocks in the Upper Cretaceous Western Series of the

Western Interior Basin have similar Ce/Ce* values to those of the Bearpaw fossils, the Western Interior Seaway -- epicontinental, shallow, and for much of the time constrained near its northern and southern apertures -- may neither have been well oxygenated nor particularly dynamic through much of the Late Cretaceous Epoch. Long-term isotopic stratification of the Western Interior seaway could be an expression of these conditions. Dysoxic conditions of the Bearpaw sea may also explain the peculiar character of the foraminifera- and mollusc-dominated Bearpaw fauna with its obviously diminished representation of other contemporary invertebrate groups.

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APPENDIX 1. Analytical Procedures

1. Sample Preparation

Fossil shells were first washed in acetone to remove any surface organic materials, then rinsed several times in distilled water. Samples of shell carbonates for analysis were obtained either by flaking off fragments of shells with a scalpel, or by using a dental drill. Aragonite is the preferred $CaCO_3$ polymorph for chemical and isotopic investigations because it records alteration more readily than calcite. Another reason for choosing aragonite is that aragonite layers of the mollusc fossils collected are much better preserved than calcite layers (see Section 3).

Quantitative Mineralogy

Aragonite is metastable under the Earth's surface conditions, and will be altered to calcite. Before chemical and isotopic analysis, all samples of shell aragonites were examined by quantitative X-ray diffraction (XRD) analysis to determine the presence and quantity of any secondary calcite, using the Davies and Hooper method (1963). The accuracy of this quantitative XRD method is claimed to be 1%.

Before a large number of samples were analyzed for stable isotopes and chemical compositions, the relationship between the secondary calcite contents, stable isotopes, and chemical compositions in the samples was investigated. Based on these data, standards for well-preserved samples for chemical and stable isotopic analyses were determined (see Section 3 for details).

Electron Microprobe Analysis

The *JEOL 8600* scanning electron microprobe (SEM) was also used to check other phases of the microscope scale which cannot be readily detected by the XRD method, and yet aid in the selection of samples suitable for analysis, especially trace-element analysis.

2. Stable Isotope Analysis

Carbon- and oxygen-isotope compositions of aragonite were determined using 100% phosphoric acid, according to the method of McCrea (1950). All values were reported relative to reference standards in the δ notation as:

$$\delta^{18}O = [(^{18}O/^{16}O)_{spl} /(^{18}O/^{16}O)_{std} - 1] \times 10^3 \quad (7.1)$$

$$\delta^{13}C = [(^{13}C/^{12}C)_{spl} /(^{13}C/ ^{12}C)_{std} -1] \times 10^3 \quad (7.2)$$

in units of per mil (‰). Where 'spl' refers to the sample analysed and 'std' to the standard used. The Peedee Belemnite (PDB) is used as the standard for $\delta^{18}O$ and $\delta^{13}C$ values of carbonate samples . Replicate isotopic analyses of aragonite indicated a reproducibility of ±0.2‰ for $\delta^{13}C$ values and ± 0.1‰ for $\delta^{18}O$ values (2σ).

Due to differences in physical-chemical properties of isotopically-substituted molecules or crystals, isotopic fractionation between two substances can occur during physical or chemical processes (Kyser, 1987). The isotopic fractionation factor between two substances A and B is defined as:

$$\alpha_{A\text{-}B} = R_A/R_B \quad (7.3)$$

Where R_A and R_B represent the ratios of heavy isotope to light isotope in substances A and B, respectively. The $\alpha_{A\text{-}B}$ value is very well approximated by the difference in δ values:

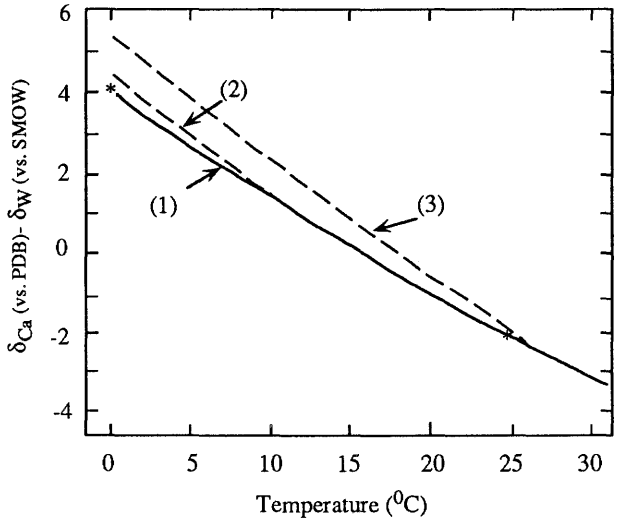
$$\delta_A - \delta_B = \Delta_{A\text{-}B} \approx 10^3 \ln\alpha_{A\text{-}B} \quad (7.4)$$

The theoretical considerations indicate that equilibrium fractionation is temperature-dependent (Kyser, 1987), i.e., $\ln\alpha_{A\text{-}B}$ varies as $1/T^2$ and $1/T$ in high- and low-temperature limits, respectively. The temperature dependence of isotopic fractionation is the theoretical basis for stable-isotope geothermometers, which have already been widely applied in many geological studies (Savin, 1982; Kyser et al., 1993).

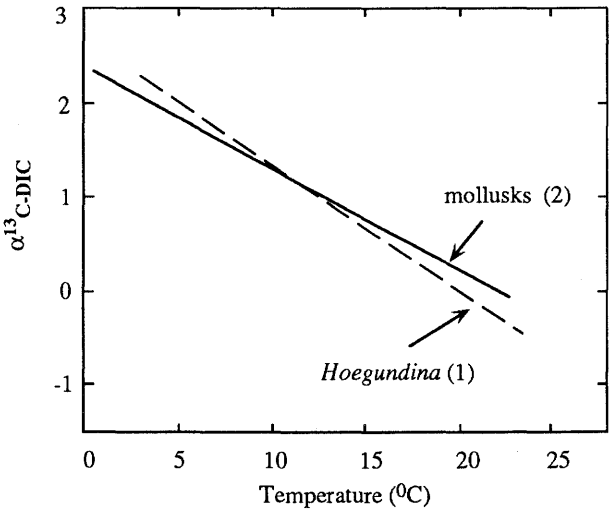
Oxygen-isotope fractionation factors between $CaCO_3$ and water have been thoroughly investigated, and experimental and theoretical results seem to be in agreement. Appendix Figure 7.1 shows oxygen-isotope fractionation factors between water and $CaCO_3$ phases at low temperatures. Fractionation factors for carbon isotopes between DIC in water and biogenetic aragonite at low-temperatures are presented in Appendix Figure 2. Carbonate-isotope fractionation between DIC in water and aragonite, deposited in isotope equilibrium with the water, showed significant temperature dependence (Grossman and Ku, 1986).

3. ICP-MS Analysis

Major- and trace-element concentrations of aragonite shells were determined by inductively coupled plasma - mass spectroscopy (ICP-MS) on 10-30 mg aliquot of powder samples, digested in analytical grade HNO_3. All samples were washed with 4 x quartz-distilled water prior to analysis. Solutions were analysed as unspiked and spiked using laboratory prepared spike solution. The accuracy among elements varied, however, usually by less than 5% for most elements and less than 10% for some elements of lower atomic weight. Major and minor elements are reported in the form of element/Ca ratio in



Apendix Fig. 1 Oxygen isotope fractionation between calcium carbonate and water as a function of temperature. Fractionation is expressed as δ_{Ca} (vs. PDB) - δ_W (vs. SMOW): (1) calcite-water (Friedman and O'Neil,1977); (2) Biogenic calcite - water (Epstein et al., 1963); (3) Aragonite - water (Grossman and Ku, 1981); * represents theoretical calcite-water fractionation (Bottinga,1968). After Anderson and Arthru (1983).



Appendix Fig. 2 Carbon isotope fractionation between calcium carbonate and dissolved inorganic carbon (DIC) as a function of temperature. Line (1) represents the data from Hoeglundina, $\alpha^{13}_{C\text{-}DIC} = 2.40 - 0.108 \times T\ (^0C)$; Line (2) represents the data from mollusks, $\alpha^{13}_{C\text{-}DIC} = 2.66 - 0.131 \times T\ (^0C)$. Modified after Grossman and Ku (1986).

the related chapters of the text.

Effects of organic matrices and FeMn-rich coatings on the REE concentrations of mollusc shells were evaluated by comparing the REE concentrations of uncleaned samples with those of cleaned samples. The methods of cleaning organic matrices and FeMn-rich coatings were from Boyle (1981), Boyle and Keigwin (1985/86). The detailed steps of procedures were: after cleaning ultrasonically in distilled water three times and removing the supernatant to remove clays and fine-grained carbonates, samples were cleaned of surface organic matter by a solution of hot (80-90^{0}C) 2 x 10 -5 M H_2O_2 in 0.1 M NaOH for 10 minutes. The supernatant was removed, and the samples were then rinsed with 4 x quartz-distilled water. Following that, they were cleaned by heating in reducing cleaning solution (0.25 M citric acid in 16 M ammonia), made up to 1 M in hydrazine (NH_2NH_2) just before the cleaning step. This reducing cleaning was continued for half an hour. All samples were washed with 10 x quartz distilled water before being put into an oven for drying.

APPENDIX 2. Major and Minor Element Concentrations of Molluscan Fossils by ICP-MS

Sample	BL(b)	BG(d)	BB(d)	BE(c)	BE(b)	BJ(a)	BR(c)	BR(a)	BCN(a)	BCN(c)	BC(b)
Na	2549	1995	1907	2242	2295	1873	2515	2173	2244	2353	2103
Mg	166	61.0	1418	162	1458	94.0	150	491	82.0	513	196
Ca	396998	386948	369384	368817	405450	362351	397399	363896	381153	378003	399867
Fe	575	99.0	870	217	1636	11364	323	703	598	2935	529
Mn	262	54.4	1401	101	510	68.6	98.7	481	77.6	239	143
Sr	3688	3582	2783	3680	5388	2893	4553	2840	2541	2546	3215
Sample	DC(e)	DC(a)	EJ(b)	EJ(a)	DS(c)	DS(b)	DN(c)	DN(a)	BS(d)	BS(f)	
Na	2710	3070	2028	2582	1872	2054	2126	2439	2363	2234	
Mg	99.0	147	277	173	199	723	97.0	65.0	92.0	79.0	
Ca	379653	389191	363339	376274	391487	364631	370770	418444	374089	376651	
Fe	365	498	1574	6507	1149	1539	696	199	400	541	
Mn	26.2	130	277	190	486	1210	34.2	37.7	53.0	54.7	
Sr	3035	2143	3855	2160	3574	2496	2478	3093	2736	2987	

Note: concentrations in ppm.