Using Geochemical Analysis to Determine Paleoclimate at the Eocene-Oligocene Boundary (35Ma) of the Lincoln Creek Formation, Western Washington.

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Abstract

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The Eocene Oligocene boundary is a critical interval in geologic history, from Eocene hothouse conditions, to Oligocene icehouse. The causes and magnitude of climatic change during this time are not well known, particularly the changes associated with terrestrial and near shore regions. While deep sea geochemical records indicate a rapid cooling of several degrees centigrade, it is difficult to correlate this data with terrestrial studies, which show a smaller temperature change based on leaf morphology studies. A link is needed between the two systems in order to determine a clear picture of the global pattern of climate change. This study investigates the validity of utilizing two geochemical techniques to reconstruct paleotemperatures in a marine environment from outer shelf/slope depths as a comparison to the deep sea records. A data set from a marine environment that actively mixes with the atmosphere should provide an intermediate setting between the deep sea and terrestrial realms. It is considerably more difficult to obtain valid data from shallower environments, due to diagenetic effects, imprecise depth determinations, low sample size, and terrestrial inputs to the marine system. However, this study shows that it may be possible to glean meaningful information about climate change from shelf/slope sea sections, and these may provide a valuable link between the terrestrial and deep marine realms.

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Introduction

Background

The Eocene-Oligocene boundary is a critical interval in geologic history between the Eocene hothouse world and the Oligocene global icehouse. The boundary represents the most recent major climatic shift, and the last major extinction of marine fauna. In the past two decades a large body of work has been produced on the details of the Eocene-Oligocene transition in both the terrestrial and marine records. Originally thought to be one Terminal Eocene Event (Wolfe, 1978), the transition is actually much more complex, involving several biostratigraphic zones, and extending from the late-middle Eocene through the early Oligocene. Fossils from Oregon and Washington indicate that there are two periods of fossil extinctions and originations (turnovers), each implying a rapid climate change. In California there are three such turnovers (Hickman, 2003; Nesbitt, 2003; Squires, 2003). There is also evidence from western Oregon floral fossils of a change from a sub-tropical to a temperate regime, based on angiosperm leaf morphology from time-equivalent plant fossils (Kester, 2001; Myers et al., 2002; Myers, 2003).

The Eocene-Oligocene boundary is placed in the lower part of chron C13r at 33.7 Ma (Berggren et al., 1995; Nesbitt, 2003). The global stratotype sections and points (GSSP) is located in the Massignano section of the Apennines, Italy, and is defined as the last appearance datum (LAD) of *Hantkenina* spp. (Pomerol and Premoli Silva, 1986; Premoli Silva et al., 1988; Berggren et al. 1995). The boundary is associated with a major (1.5‰) shift in oxygen isotope ratios, defined as Oi-1 by Miller (1992). This shift

has been interpreted as a major change in climate, from a rapid drop in global temperature and the first growth of the Tertiary/Cenozoic Antarctic ice sheet (Kennett, 1977; Miller, 1992; Zachos et al., 2001).

The causes of the Eocene-Oligocene climate shift are under some debate, primarily involving the growth of the Antarctic ice sheet, and its effect on global climate. There has been conflicting evidence over the average temperature change of the transition, with estimates from a decrease of 16°C initially (Miller, 1992) to as little as 4°C (Zachos, 2001) in more recent work. All the initial paleotemperature data was obtained from oxygen isotopic signatures from microfossils (Miller, 1992). The marine data are from benthic and planktonic organisms obtained from deep-sea cores, so that only the open ocean temperatures are known. These data indicates a 4-6°C temperature drop in global ocean temperatures across the Eocene-Oligocene boundary (Figure 1), followed by another 4°C drop in the early Oligocene (Miller, 1992; Zachos *et. al*. 2001). The ice accumulation signature in the oxygen isotope record is larger than the decreasing temperature signals (Figure 1) except for the first major excursion at the boundary.

The fossil record shows a significant change in climate, based on turnover micro- and macro- organisms. Faunal turnover indicates a narrowing of global tropical belts around the Eocene-Oligocene boundary in Oregon. There are two major fossil turnover events, first from the tropical fauna of the Cowlitz Formation to the turnover fauna of the Keasey Formation (36.5 Ma) and secondly from the latter to the temperate recovery fauna found at the Pittsburg Bluff, Eugene and Scappoose Formations (32.5 Ma) (Hickman,

2003). This indicates significant cooling may have started several million years before the Eocene-Oligocene boundary in the Pacific Northwest. Farther south, in California, an additional turnover at 28.5 Ma was noted (Squires, 2003), coinciding with Miller's (1992) third isotopic excursion.

The uncertainty in the magnitude of temperature change at the Eocene-Oligocene boundary is in part due to the way in which ice growth effects are seperated from oxygen isotope data, in order to use it as a temperature proxy. As temperature drops, ocean water becomes more enriched in the heavier isotope, ^{18}O. The same enrichment occurs as the light oxygen isotopes (^{16}O) are sequestered in terrestrial ice. Calcite secreting organisms incorporate oxygen into their shells directly from seawater, thus preserving the isotopic ratio of the water (Criss, 1999). Some organisms directly record the ratio, while others produce a vital effect which shifts the ratio a fixed amount from that of the water. The highly predictable change in oxygen isotope ratios can be used to infer changes in temperature by comparing $^{18}O/^{16}O$ ratios of fossils. The derived temperatures can then be compared to present oceanic conditions.

The problem in interpreting the data from fossils arises from the inability to distinguish between oxygen isotope variations due to globally decreasing water temperatures and the impact of increasing ice volume. In *both* cases, the seawater, and the animals that precipitate their shells from the seawater, become enriched in ^{18}O relative to starting conditions. This ambiguity is easily resolved if ice volume is known, as is the case today, and in earlier times, such as the early Cretaceous, when there was no global ice. However, the Eocene-Oligocene transition lies within the period of time when the

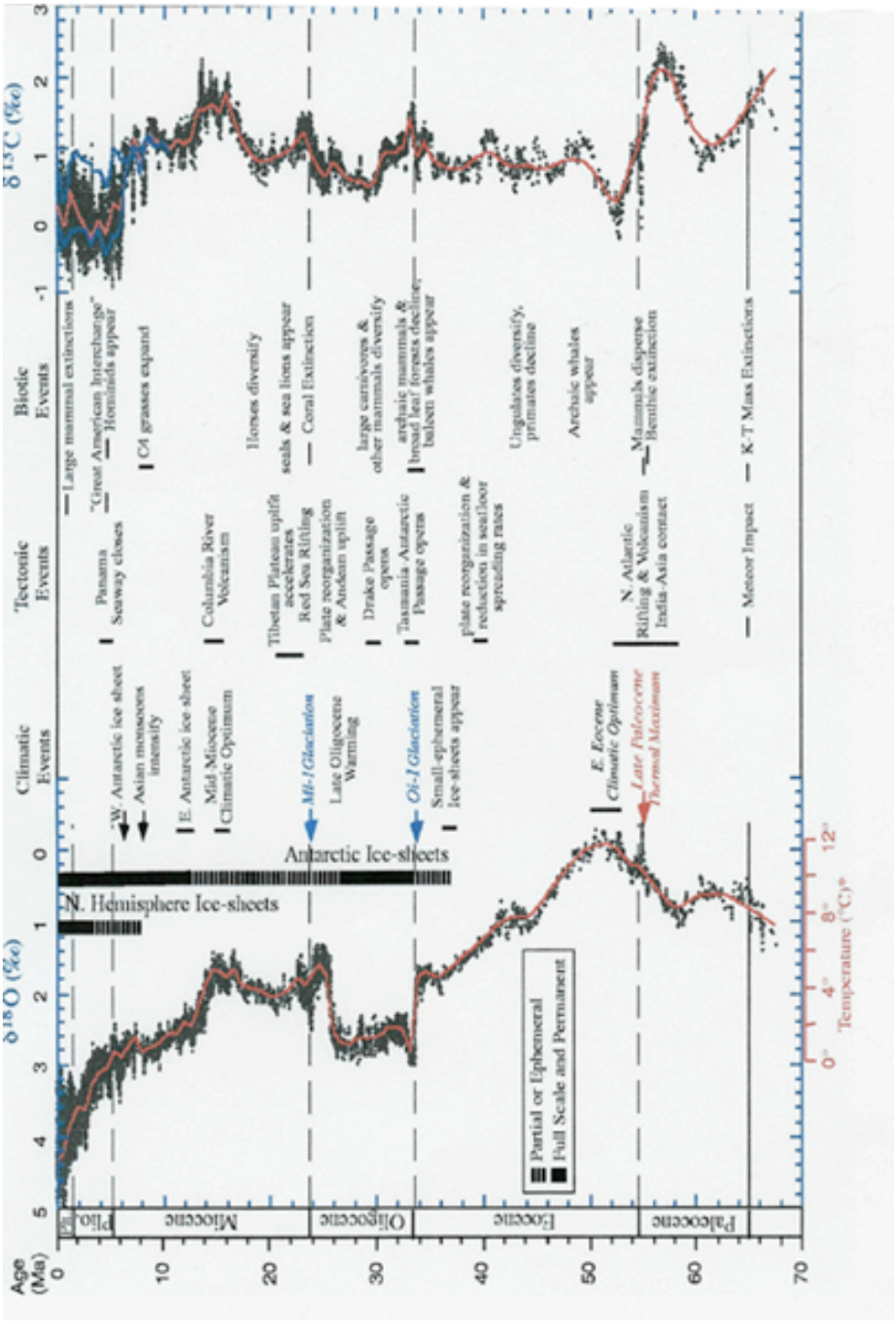


Figure 1. Global Deep Sea Stable Isotopic Records. Oxygen and carbon curves based on data from >40 DSDP and ODP sites, from Zachos et al. (2001).

Antarctic ice sheet first began developing in the Cenozoic. The variable amounts of ice present and the lack of a realistic ice sheet growth model for the Cenozoic make it difficult for scientists to agree on which part of the isotopic signal belongs to ice growth, and which to temperature change. However, new methods of determining ice effects on the oxygen isotope system have recently been proposed (Rosenthal et al., 1997; Lear et al., 2000). This geochemical technique involves measuring the Mg/Ca ratios in fossil shells, and is dependant on temperature, but independent of ice volume. This would allow for the separation of the two signals within the global oxygen isotope change.

A second issue with the interpretation of climatic change is the lack of data from shelf/slope depth. Shallow marine environments are coupled more strongly with air temperature, since in the upper mixing zone of the ocean, the water is in direct contact with the atmosphere. Because the upper layer of the ocean is actively exchanging gas with the atmosphere, it is closer to chemical and temperature equilibrium, and should provide a more precise model of climate change. Currently the only high resolution oxygen data available is from deep sea cores, along with some paleontological studies from terrestrial sections. Terrestrial sections are not obtained from isotopic data, while deep water samples do not accurately reflect the timing or magnitude of temperature change at the surface. An intermediate proxy, such as a shelf/ upper slope section, provides the link between the deep ocean and the land that is needed to determine the cause of the Eocene -Oligocene transition.

This Study

The current study used fossils of the Lincoln Creek Formation of western Washington to create an oxygen isotope record of the Eocene-Oligocene boundary in the Pacific Northwest. This study proposes possible solutions for both of the major problems in interpretations of paleotemperature stated above. By using fossils from a upper to middle bathyal depth to obtain isotopic data, the link between deep sea and terrestrial records is bridged, and by using new geochemical systems, such as Mg/Ca ratios, the problem of ice growth and fluctuation can be removed from the oxygen isotopic signature. This project utilized fossils from museum holdings, collected from the marine sedimentary rocks of the Lincoln Creek Formation, exposed along the Canyon River and the Middle Fork of the Satsop River, as well as the Pe Ell-Doty section, south of the Olympic Mountains, western Washington (Figure 2). Faunal assemblages from these sections of the Lincoln Creek Formation indicate deposition on the slope at upper to middle bathyal depths (Rau, 1957; Rau, 1966; Armentrout, 1973; Ingle, 1980; McDougall, 1980). Paleoenvironmental analysis shows theses sediments were deposited in an open coastal setting, and not and embayment.

There is currently very little oxygen isotope data from the North Pacific Ocean, and none from marine slope environments. Nesbitt (2003), Hickman (2003) and Squires (2003) have shown that there is a major shift from warm water, shallow marine faunas in the mid-Eocene to cool water taxa in the early Oligocene along coastal California, Oregon and Washington. Nesbitt's (2003) study utilized taxon diversity and numerical dominance of molluscan fossils from the Lincoln Creek Formation, and other co-eval

formations in western Washington to pinpoint times of major environmental perturbations.

For the current study, fossils were analyzed from the Lincoln Creek Formation of western Washington, from a total of four sections (Figure 3). Three sections were marine slope sediments, while the other two were from an inner shelf setting, based on faunal assemblages (Rau, 1958; McDougall, 1980). To determine relative sea level changes over the period of deposition, and to better understand the depositional environment, grain size analysis was obtained for the Canyon River section. Both micro- and macro-fossils were utilized in this study, based on abundance in the section and previous work (Rau, 1966; Armentrout, 1973). Three different genera of benthic foraminifera were used primarily in order to show internal consistency and for comparison to previous studies. Fossil bivalves of the genus *Lucinoma* were also tested due to their abundance in the sections.

Using Mg/Ca ratios in paleoceanography was first suggested by Rosenthal et al. (1997), who found that the incorporation of Mg into carbonate structures is temperature-dependent. Mg/Ca ratios do not change based on ice volume, however, since neither is a component of ice. By acquiring both oxygen and Mg/Ca ratios from the same samples, the effects of ice on the record can be determined, assuming secular changes in Mg/Ca ratios through time are known.

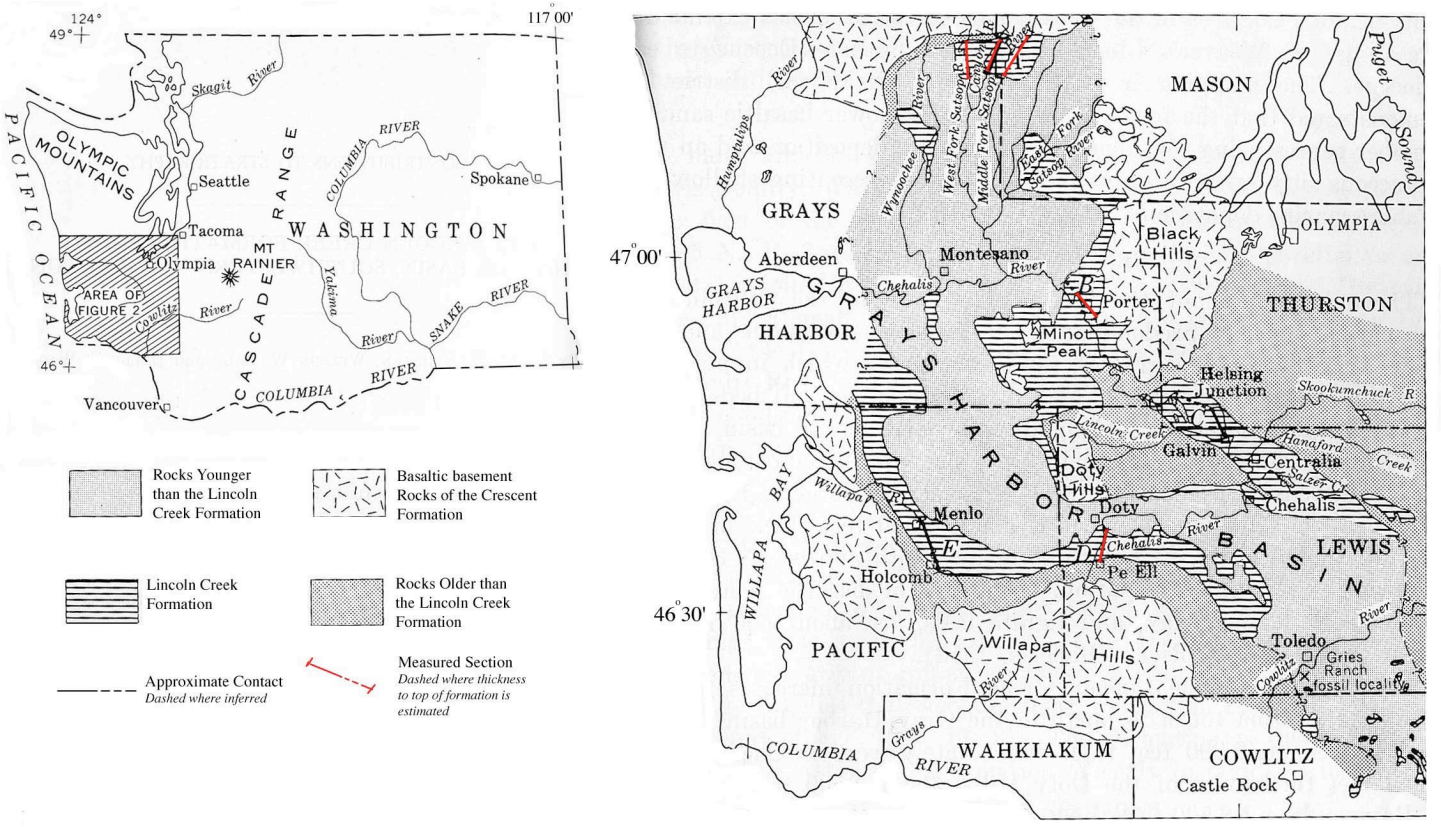


Figure 2: Mapped area of Lincoln Creek Formation, western WA, and associated rocks. Modified from Beikman et al. (1967).

The Lincoln Creek Formation

General Stratigraphy

Rocks of the Lincoln Creek Formation were first described by Arnold (1906a) as marine sediments from outcrops along approximately one mile of Highway 9 both north and south of Porter (Figure 2). These were named the Porter Shales, and Arnold (1906b) correlated them with the San Lorenzo Formation of California based on fossil assemblages.

The Lincoln Formation, as it was first named, was defined by Weaver (1912) for outcrops along the Chehalis River and Lincoln Creek, Thurston County, Washington. The formation was later redefined by Weaver (1937) to include numerous stratigraphic sections along the Chehalis River, in the area between Centralia and Porter, including Arnold's (1906a) Porter Shales. Weaver's (1912, 1937) definition of the Lincoln Formation was based primarily on molluscan assemblages. He believed the formation to represent the entire Oligocene in Washington. Based on benthic foraminifera, Snaveley et al. (1958) showed that the Lincoln Formation spans the time period of Late Eocene to Early Miocene. Beikman et al. (1967) renamed the Lincoln Formation as the Lincoln Creek Formation, to avoid conflict with another formation already named Lincoln.

The type section of the Lincoln Creek Formation (Weaver, 1912; Beikman et al., 1967) is along the Chehalis River and is normally called the Galvin Section in the literature. The Galvin Section consists of approximately 400 m. of tuffaceous silt and sandstone, with tuff beds, and erosionally resistant calcite cemented beds. Additional

outcrops of the Lincoln Creek Formation were mapped by Snavely et al. (1958) in the Centralia-Chehalis coal district.

Armentrout (1973, 1975) defined two molluscan stages and six in the Lincoln Creek Formation (Figure 3). A high-resolution chronostratigraphy of the sequences has been generated from paleomagnetic signatures tied to micro- and macrofossil biozones (Prothero and Armentrout, 1985; Prothero and Thompson, 2001; Prothero et al., 2001).

The Lincoln Creek Formation includes rocks that extend from 660 to over 3000 m. in stratigraphic thickness, and is thickest towards the western margin of the outcrop area (Armentrout, 1987). The formation overlies rocks of Middle Eocene age, and the lowermost unit is a thin basaltic sandstone member, representing continental or near-shore deposition. Most of the formation consists of tuffaceous silty-sandstone and siltstone units originally interpreted as representing shallow-water marine deposition (Beikman et al., 1967). The eastern outcrops of the formation are mostly composed of tuffaceous sandstone and conglomerate, while the western sections are dominated by finer-grained sandstone and siltstone. These indicate both a deepening depositional environment to the west and indicate a subsiding basin creating to an apparent local transgression (Armentrout, 1987). The Lincoln Creek Formation is overlain by the Astoria Formation of early Miocene age or the Montesano Formation of late Miocene age (Armentrout, 1973; Prothero, 2001). Armentrout (1987) described the Lincoln Creek Formation as part of sequence III in a series of unconformity-bounded sequences stretching across all of Southwestern Washington (Figure 3).

There is also evidence of cold methane seep deposits in some of the deeper water sections, indicated by unique low oxygen faunal assemblages and deposits of calcite in the form of glendonite (Peckmann et al., 2002). Glendonite is a stable pseudomorph after the mineral ikaite ($CaCO_3 \bullet 6H_20$), which forms as submarine columns and chimneys in certain conditions of water temperature in the range of –1.9°C to 7°C, and in the presence of high concentrations of organic carbon. The type examples of ikaite are in fjords in Greenland (DeLurio and Frakes, 1999), but glendonite is also commonly found associated with fossil cold seeps (Campbell et al., 2000). The presence of glendonite throughout the section serves as a second, non-biogenic proxy for bounding temperatures, and also indicates that there were no rapid fluctuations in temperature, otherwise the ikaite would have dissolved.

Areas of Study

Five stratigraphic sections of the Lincoln Creek Formation were chosen for this project; the Satsop River area, consisting of outcrops along the Canyon River, the Middle and West Forks of the Satsop River, and road cut exposures of the Porter Bluff and Pe Ell – Doty sections (Figure 3). The three Satsop River sections were used extensively, while the Pe Ell – Doty section provided very little data. The Porter Bluff section is included as reference, but no isotopic data were collected from it.

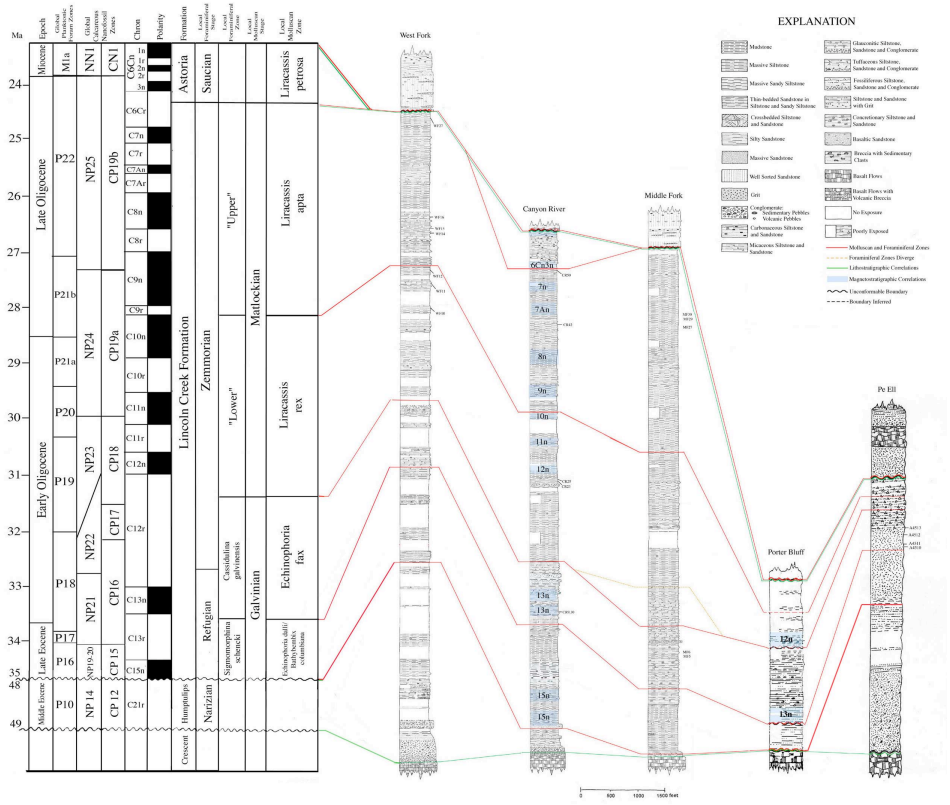


Figure 3. Compilation of stratigraphic data and correlations for the Lincoln Creek Formation. Compiled and modified from: Armentrout (1975), Berggren et al. (1995), Prothero et al. (2001), Prothero and Armentrout (1985), and Strong (1966).

Satsop River Area

The Satsop River sections are extremely similar, and geographically close, cropping out within a 3-mile area (Figure 2). Rau (1966) correlated the sections with each other using local lithological members, which he named T1-1 through T1-9 (Table 1), and with other sections of the formation based on foraminiferal zones. The Satsop River sections are by far the longest, and most complete of the formation, with few apparent unconformities, making them the best for most research purposes. For this study, the isotope data from fossils collected in the three sections was combined into one data set. In the Satsop River area, the Lincoln Creek consists of almost 3000 m. of tuffaceous material ranging in size from mudstone to sandstone (Figure 3). Table 1 summarizes the stratigraphy of the Satsop River Area sections of the Lincoln Creek Formation.

Pe Ell – Doty

The Pe Ell – Doty section outcrops along the Chehalis River in between the towns of Pe Ell and Doty, Washington (Figure 2). Here, the Lincoln Creek Formation is composed of over 660 m. of tuffaceous and concretionary sandstone and siltstone. The most detailed stratigraphic sections were measured and described by Strong (1966). The Lincoln Creek Formation at the Pe Ell-Doty section overlies marine sedimentary rocks of the Humptulips Formation of middle Eocene age (Armentrout, 1975) (Figure 3). Its basal section (20 m.) is a highly fossiliferous, medium grained basaltic sandstone, with thin

Table 1. Summary of the Stratigraphy of the Satsop River sections of the Lincoln Creek Formation. From Rau,1966.

Member Number	Stratigraphic Thickness	Lithologic Description
T1-9	160 - 270 m.	Massive siltstone, containing almost no sand, and almost no bedding. Member thins to the east due to onlap of younger rocks.
T1-8	530 - 800 m.	Massive siltstone and sandy siltstone, interbedded with sandstone beds. This member is distinct from the surrounding members due to a much higher percentage of sand and more distinct bedding. There are concretionary layers, as well as scattered concretions throughout the section, and in the West Fork and Canyon River sections there is a fossiliferous, glauconitic bed low in the member.
T1-7	300 - 460 m	Massive siltstone member containing thinly-bedded sandstone units. A~30 m. thick calcite bed in the central portion of the member in the Little River section, which was not used in this study.
T1-6	100 - 300 m.	This bedded member contains sandstone and sandy siltstone interbedded with massive siltstone layers. The base is fossiliferous sandstone, and most of the rock is tuffaceous.
T1-5	200 – 400 m.	Fine-grained material, mostly massive with a few scattered concretions. In the West Fork section sandstone beds are more common, and the massive siltstones are sandier.
T1-4	170 - 330 m.	Thick, poorly-sorted beds of conglomerate and sandy grit interbedded with massive, highly tuffaceous siltstone beds. It is not well developed in the three research sections
T1-3	230–370 m.	Poorly sorted material, with concretionary layers and sandstone interbedded with siltstone. The larger particles are composed mainly of glass and pumice, and basalt, and fossils are scattered through the member.
T1-2	260 - 540 m.	Massive tuffaceous siltstone containing scattered concretions. Near the top of this member is massive mudstone or, in the West Fork section, interbedded sand and mudstone
T1-1	35 m.	Fossiliferous basaltic sandstone

lenses of basaltic and pumice pebble conglomerate. The sediments fine upwards into 630 m. of sandy siltstone, which becomes increasingly sandy, to sandstone at the top. The Lincoln Creek Formation here is unconformably overlain by rocks of Miocene age, probably Montesano Formation (Armentrout, 1975).

Porter Bluff

The Porter Bluff section spans the same age range as the type Galvin section, but also includes some older rocks of Eocene age (Beikman *et. al.,* 1967; Armentrout, 1973). The section consists of approximately 1000 m. of fine to medium grained, tuffaceous, silty sandstone, with interbedded medium to coarse-grained sandstones and thin concretionary layers. The lowermost 35 m. is composed of conglomeratic, basaltic sandstone, which unconformably overlies the Crescent Basalts. The section fines upwards, and is unconformably overlain by Miocene sediments, most likely Astoria Formation or possibly Montesano Formation (Armentrout, 1973) (Figure 3).

Fossil Assemblages and Depositional Depth of the Lincoln Creek

Depth assessments of the rocks of the Lincoln Creek Formation are based on lithologies and faunal assemblages (Appendix 3). Rau (1951, 1966) interpreted the foraminiferal assemblage to represent an open ocean upper bathyal depth, which he defined as 2000 to 650 feet in depth. McDougall (1980) later refined the depth assemblages, and modified Mallory (1959) and Rau's (1966) zonal schemes for Washington. Relevant depth ranges are shown in table 2 (McDougall, 1980).

Table 2. Depth ranges of marine shelf and slope zones. From McDougall (1980)

Outer Neritic	100-200 m.
Upper Bathyal	200-600 m.
Middle Bathyal	600-2000 m.

Her modifications place the Canyon River section ranging from 200 to 2000 meters in depth (upper to middle bathyal) over the Eocene –Oligocene boundary, and the Middle Fork section ranging from 100 to 2000m (outer neritic to middle bathyal) over the same age (see Appendix 3). Both sections range from upper bathyal to middle bathyal through the Oligocene, with the Middle Fork section shallowing into outer-neritic at points.

The depositional depth of the Lincoln Creek sediments is extremely important for evaluating the significance of this study. If the section represents the upper mixing zone of the ocean (upper bathyal or neritic) then water temperature should be coupled very strongly with atmospheric change. However, if the section is of intermediate depth, the link between the two will be much weaker. Accordingly, the upper-middle bathyal depths (200-2000 m) determined from foraminiferal studies are largely too deep to represent the surface mixing zone. But it has been suggested that foraminifera may not accurately represent depth ranges in colder water (Armentrout, 1973). Depths based on molluscan assemblages were shallower that those derived from foraminifera previously (Rau, 1958, 1966). Cole (1957) showed that foraminiferal depth distribution changes greatly based on changes in latitude. The foraminiferal depth evaluations used by Rau

(1958, 1966) based on studies of modern foraminifera faunas from southern California, a much warmer environment. Subtropical faunas are expected to occur at shallower depths as water temperatures cool, or as latitude increases (Cole, 1957), and taking into account this pole-ward emergence the sections of the Lincoln Creek may indeed be shallow enough to be directly coupled with atmospheric processes. For this study, the Satsop River sections are considered upper-middle bathyal, based on the study by McDougall (1980) but with a depth range that cannot be constrained enough to determine if the depositional environment was upper mixing zone or intermediate zone ocean.

Zonation and Age Correlations

The age of the Lincoln Creek Formation ranges from Late Eocene to Miocene. Rau (1958, 1966) recognized the Refugian and Zemmorian benthic foraminiferal stages in the Lincoln Creek Formation. These stages were originally defined from assemblages from southern California (Mallory, 1959). Rau (1958) identified two foraminiferal zones within the Refugian stage, the *Sigmomorphina schencki* Zone and the *Cassidulina galvinensis* Zone, and he separated the Upper and Lower Zemmorian Stages. McDougall (1980) showed that these definitions and correlation with type Refugian and Zemmorian zones were problematic, in that they were based on paleoecologically diverse assemblages. Subsequent paleontological investigations have not been performed to resolve these problems, however, more recent paleomagnetic studies (Prothero, 2001) have helped correlate the Lincoln Creek Formation to both the California zones and the

global time scale and have shown that the Refugian and Zemmorian zones are time transgressive up the west coast of the United States.

Armentrout (1975) erected two molluscan stages, the Galvinian Stage and the Matlockian Stage, and six molluscan zones, *Bathybembix columbiana, Echinophora dalli, E. fax, E. rex, E. apta*, and *Liracassis petrosa* in the Lincoln Creek Formation (Figure 3). Both foraminiferal and molluscan zonation schemes indicate that the Lincoln Creek Formation ranges from late Eocene to early Miocene in age. Magnetostratigraphic studies of the Canyon River section (Prothero and Armentrout, 1985) and of the Porter Bluff section (Prothero *et. al*., 2001) support this.

The molluscan zones used in this report differ from Armentrout (1975) in several ways. Firstly, the zones named *Echinophoria rex* Zone and the *E. apta* Zone have been renamed the *Liracassis rex* Zone and the *L. apta* Zone, respectively, due to improper initial taxonomic identification (Nesbitt, 2003). Secondly, based on a taxonomic study, Nesbitt (2003) indicated that the two oldest zones, the *Bathybembix columbiana* Zone and the *Echinophoria dalli* Zone were in fact contemporaneous. Armentrout (1975) placed the type section for the *B. columbiana* Zone in the Keasey Formation in Rock Creek, Columbia County, Oregon, and the type section for the *E. dalli* Zone was placed in the Pe Ell – Doty section. Molluscan taxa that define the *B. columbiana* Zone are a deeper, colder water assemblage, and those of the *E. dalli* Zone are representative of an inner shelf assemblage. Nesbitt (2003) argued that the two zones are facies-dependent, and should be merged into one temporal unit. Correlation compilations of molluscan and magnetic zones in this report (Figure 3) agree with that finding. If the two zones were

not the same age, then chron C15n would be located in the *B. columbiana* Zone, not in the *E. dalli* Zone of the Canyon River section, as reported by Prothero et al. (2001).

While the Eocene-Oligocene boundary is well preserved in the Lincoln Creek Formation, more detailed correlation with a global scale has been difficult, due to the fact that the local zonations based on fossils are facies-dependent, as well as time-transgressive (Prothero, 2001). But studies of rare planktonic microfossils and paleomagnetism studies have allowed precise (to 100,000 years in places) correlations to the global time scale of Berggren et al. (1995)(Prothero, 2001). The magnetostratigraphic correlations done by Prothero and Armentrout (1985), Prothero (2001) and Prothero et al. (2001) have been some of the most critical factors in correlating the Lincoln Creek Formation. Prothero and Armentrout (1985) first described the magnetostratigraphy of the Lincoln Creek Formation in the Canyon River Section. Due to the unique length and pattern of chrons C13r and C12r, which were present in the section, they hypothesized that the formation began at chron C15n. This was supported by calcareous nanoplankton data (Prothero and Armentrout, 1985) which show that the Canyon River Section spans chrons C15n through C6Cr, and is continuous. Comparison to the Berggren et al. (1995) time scale gives the Canyon River Section an age range of 35 Ma to 24.3 Ma. Prothero et al. (2001) correlated the Porter Bluff Section to the Canyon River Section, and thus to the global time scale (Berggren et al., 1995). By comparing magnetostratigraphy and biostratigraphy, they found that in the region of the Porter Bluff Section where magnetostratigraphic data was collected, it is composed of three unconformity bounded sequences, and contains chrons C13n, C12r, and C12n, and the measured part of the

Porter Bluff Section spans an age of 34 to 30.8 Ma. Magnetostratigraphic correlations of the uppermost part of the section were not possible. Further, Prothero and Thompson (2001) correlated the Refugian benthic foraminiferal stage of California with the global time scale using magnetostratigraphy, thus allowing correlations between the California sections and those of the Pacific Northwest.

In western Washington the Eocene–Oligocene boundary falls within the lower Lincoln Creek Formation. Here the Refugian Stage begins about 2 million years later, and ends 1 million years after the type section in California (Prothero and Thompson, 2001). This places the actual Eocene-Oligocene boundary, based on magnetostratigraphy, within the Refugian foraminiferal stage in the Lincoln Creek Formation. The major climatic shift and molluscan turnover events occur at the Refugian-Zemmorian boundary, which in Washington, is in the Early Oligocene (Hickman, 2003; Nesbitt, 2003).

Geochemical Analysis

Oxygen Isotope Analysis

Obtaining paleotemperatures from carbonate oxygen isotopes is based on changes in incorporation of different oxygen isotopes into shell $CaCO_3$ as the temperature changes. Oxygen exists in three different isotopic forms, ^{16}O, ^{17}O, and ^{18}O. ^{16}O is the most common, comprising ~99.9% of the earth's oxygen, while ^{18}O makes up only 0.1%. ^{17}O makes up less than 0.01%, and is not used in paleotemperature determination. As marine organisms precipitate $CaCO_3$ shells, they incorporate dissolved CO_2 from the surrounding ocean water, and record the isotopic ratio of the water at that time. Some organisms, such as mollusks and echinoderms, incorporate isotopes in equilibrium with seawater ratios (Criss, 1999). Others, like some foraminifera genera, change the ratio a small, but constant amount as they form their tests. This change is called a vital effect, defined as an isotope fractionation that is biologically mediated (Grossman, 1987). As global temperature drops, water with lighter oxygen isotopes evaporates preferentially, and the ratio of ^{18}O: ^{16}O increases in the remaining seawater and, consequently, in the carbonates. Preferential incorporation of the light isotopes of oxygen into ice leaves relatively higher amounts of ^{18}O in the remaining water. By comparing the ratio of the sample to a known value, such as the standard mean ocean water (SMOW) ratio or the Pee Dee Belemnite (PDB) standard, a delta value ($\delta^{18}O$) can be determined using equation 1 (Criss, 1999).

$$(1) \qquad \delta^{18}O = \left(\frac{(^{18}O/^{16}O_{sample} - {}^{18}O/^{16}O_{Std})}{{}^{18}O/^{16}O_{Std}} \right) \times 1000$$

This value can then be converted to an actual water temperature using equation 2 (Criss, 1999)

$$(2) \qquad t°C = 16.9 - 4.38(\delta_{cc} - \delta_w) + 0.14(\delta_{cc} - \delta_w)^2$$

where δ_{cc} is the delta value of CO_2 released from the sample carbonate and δ_w is the delta value of CO_2 precipitated from inorganic carbonate in equilibrium with seawater of the same age as the sample at 25°C. In order to calculate δ_w several factors need to be accounted for: 1) The amount of isotopic signal due to ice volume changes, 2) calculating a value for vital effects from the organism, and 3) estimating any secular changes in $\delta^{18}O$ and ocean chemistry throughout geologic time.

The concept of using oxygen as a paleothermometer was originally proposed by Urey (1947), and the carbonate-temperature calibration curve was defined by McCrea (1950) and refined by Epstein et al. (1953). The original equation has since been adapted slightly to equation (2) above, as measurement techniques became more refined. The PDB standard is the more commonly used for biogenic carbonate and paleontological studies, while SMOW is commonly used in modern oceanographic studies (Criss, 1999).

Complications with the Oxygen Isotope System

A major complication in the carbonate isotope system, and possibly the hardest to constrain quantitatively, is diagenesis, chemical alteration and reprecipitation of the carbonate over time. Diagenesis occurs with burial of sediments, and generally increases with depth and age (Schrag et al., 1995). All benthic and high latitude planktonic biogenic carbonates exhibit a decreasing $\delta^{18}O$ as secondary carbonate is precipitated. At lower latitudes, warmer water carbonates undergo a more complex diagenetic process, with $\delta^{18}O$ values first rising, and then falling as the carbonate undergoes diagenesis (Schrag et al., 1995). This difference in diagenetic alteration is due to carbonates in cold water and benthic settings forming with a higher $\delta^{18}O$ than the surrounding seawater, while warmer water carbonates form with a $\delta^{18}O$ that is higher than surrounding seawater. As pore waters alter the carbonate, the $\delta^{18}O$ falls or rises to reach equilibrium (Schrag et al., 1995). In the case of planktonic foraminifera, in order to create a quantitative model to determine which process of alteration has been followed (falling or rising oxygen ratios to reach equilibrium), factors such as sedimentation rate, the equilibrium calcite curve, and recrystallization rate of the carbonate all need to be accounted for (Schrag et al., 1995).

There are several methods for potentially recognizing diagenetically altered carbonate, but there is no quantitative way to distinguish the diagenetic isotopic signal from that of the actual temperature and ice data, unless the precise degree of alteration is known (Criss, 1999). X-ray diffraction (XRD) analysis can show diagenetic alteration of

the metastable aragonite form of carbonate, since secondary carbonate is always in the form of calcite (Grossman and Ku, 1986). XRD is accurate to 95%, i.e. a bulk aragonite sample would have to be less than 5% altered in order to pass as unaltered material. However, XRD will not indicate diagenesis in calcite fossils, since primary and secondary calcite are indistinguishable (Grossman and Ku, 1986). In studies of Quaternary and late Cenozoic carbonates, the concentration of Sr in the carbonate structure can be used to estimate the degree of recrystallization (Schrag et al., 1995). In biologically precipitated carbonate, Sr concentrations are higher than in the surrounding pore waters. As diagenesis proceeds, the Sr is leached out of the material by the depleted pore waters via diffusion (Schrag et al., 1995). If the global oceanic Sr concentration is known, the amount of diagenesis can be estimated from the Sr concentration in the shell. However, the Sr concentrations of the oceans have changed through time, so this method is applicable only in more recent times (Stanley and Hardie, 1998; Lear et al., 2000). Similar relationships exist with other trace elements as well. Veizer and Fritz (1976) suggested using Mn concentrations to detect alteration, based on the same biological enrichment effects described for Sr in carbonates. Again, as pore waters alter the carbonate, Mn will be leached out. It has also been shown that uranium concentrations will rise with diagenesis, (Criss, 1999) creating another possible detection method. However, the same problems with temporally variable concentrations apply. There is no defined way of determining whether diagenesis has occurred or the extent of diagenesis for older calcite samples. There is also no way to entirely exclude diagenesis as a possible cause of discrepant data in a study such as the current one. One possible

method for determining if oxygen data is valid is to compare the carbon and oxygen ratios of a carbonate sample. Carbon and oxygen isotope ratios have been shown to covary in biologically precipitated carbonates (Fairbanks et al., 1982), however, carbon is a more stable component of calcite than is oxygen. So if $\delta^{13}C$ is wildly off from expected values due to apparent diagenesis, then it is safe to assume that oxygen is also altered. The only data that are entirely reliable are data where it can be argued that no alteration has occurred through several lines of evidence (Criss, 1999).

A second complication with the oxygen isotope system is the vital effects that certain organisms impart on the $\delta^{18}O$ ratio of their shells (Grossman, 1987). Vital effects are common in chemical analyses of biogenic minerals. For an extant species, or an extinct species with extant relatives, studies can be done on the living species to establish the amount of isotopic change due to vital effects of the organism. This effect can then be corrected for in the paleo-data by simply subtracting the isotopic shift from the data set (Criss, 1999). Studies have shown that animals such as mollusks and brachiopods do not produce any measurable vital effect on oxygen isotopes (Dando and Spero, 1993; Criss, 1999; Rodland et al., 2003). The vital effects of foraminifera vary between genera, with only very small differences between species of the same genus (Erez, 1978; Grossman, 1987; Spero and Williams, 1989; Volkmann and Mensch, 2001). Symbiont bacteria have also been shown to alter stable isotopic values, but seem to have a major effect only on carbon ratios, not oxygen ratios in the bivalve genus *Thyasira* (Dando and Spero, 1993). No studies have been done on the shells of *Lucinoma*, but it is assumed

that symbiont bacteria will behave in the same way. In the case of this study, the vital effects of all genera of foraminifera used are known (Grossman, 1987), making corrections possible.

The third complication with using the carbonate-temperature relationship to determine paleo-temperature arises from secular changes in oceanic oxygen concentration through time. These occur in part due to fluctuations in global ice volume. $\delta^{18}O$ has been shown (Shackleton, 1987) to increase 0.25‰ for every 1°C decrease in temperature, and also increase as continental ice volume increases by 0.1‰ for every 10 meters of sea level change (Zachos et al., 2001). However, since the two systems are related, it is difficult to separate the two signals. In the Quaternary, when global ice volume is known, the problem is easily solved, but the farther back in time the more difficult it is to determine global ice volume. During the early Oligocene the first permanent ice sheets were forming on Antarctica, with the timing of their first formation partially constrained by isotopic studies (Shackleton and Kennett, 1975; Kennett, 1977; Miller et al., 1991; Zachos et al., 1992; Zachos et al., 2001). Growth of the Antarctic ice sheets associated with the Oi-1 event has been constrained to a period between 33.6 and 33.48 Mya, with periods of rapid growth caused by low eccentricity of the earth's orbit (Kennett and Exon, 2003; Mallinson et al., 2003). However, since the precise timing and magnitude of glaciation is generally unknown, qualitatively separating the two effects out of the data set is not possible to any high degree of certainty at this time.

Carbon and oxygen isotope ratios have been shown to covary in biologically precipitated carbonates (Fairbanks et al., 1982), indicating a process not linked to

physiology, since respiration processes only affect carbon ratios (Spero et al., 1991). The cause of this covariance is believed to be the concentration of CO_2 in ocean water (Spero et al., 1997). $\delta^{18}O$ decreases with increasing concentration, so in times when the ocean pH is higher, such as in glacial periods, $\delta^{18}O$ will be lower (Sanyal et al., 1995). Rates of tectonic activity and weathering are additional causes of fluctuations in ocean chemistry which can affect pH, and thus the relationship between $\delta^{18}O$ of seawater and temperature.

In order to produce quantitative paleotemperature data from fossil carbonate all of theses issues, diagenesis, vital effects, ice volume, and seawater chemistry, need to be addressed (Pearson et al., 2001). But even if these signals cannot be readily removed or compensated for, qualitative conclusions may still be obtained through comparison with other isotope studies.

Oxygen Isotope Record of the Eocene-Oligocene boundary

The first reported marine oxygen isotopic data from the Eocene-Oligocene boundary were derived from deep water benthic foraminifera from off the coast of California (Miller, 1992). The data showed an increase in global $\delta^{18}O$ of 1‰ at the Early/Middle Eocene boundary and again at the Middle/Late Eocene boundary. These data indicated a further increase of 1‰ at the earliest Oligocene (called Oi-1). At the time of Miller's (1992) study, the inferred temperature change associated with the change in oxygen was -5°C for each 1‰ change, giving a total decrease of 15°C for deep waters in the Eastern Pacific margin from the Early-Middle Eocene boundary to the earliest

Oligocene. Miller (1992) interpreted this change in temperature to be the cause of the 'Terminal Eocene Event' named by Wolfe (1978) for the extinction of tropical flora at the Eocene-Oligocene boundary.

How much of the isotopic change is due to temperature fluctuation and how much to ice sequestration during the Eocene is still under debate due to uncertainties about the timing of Antarctic ice sheet formation. The first major Antarctic glaciations occur in conjunction with Oi-1, and have significant effects on the isotopic record (Shackleton and Kennett, 1975; Kennett, 1977; Miller et al., 1991; Zachos et al., 1992; Zachos et al., 1994; Zachos et al., 2001). Temperature fluctuation estimates have ranged from 15°C total, with 8°C after the start of ice sequestration (Miller, 1992; Zachos et al., 1994) down to 4°C or less at the Eocene-Oligocene boundary (Zachos et al., 2001). Based on taxonomic studies of the faunal changes, the idea of a single Terminal Eocene event has been revised to a step-wise species turnover involving several stages (Ivany et al., 2000; Hurly and Fleugeman, 2003; Nesbitt, 2003; Oleinik and Marincovich, 2003). These studies on Cenozoic marine sections along the west coast of North America show species turnovers occurring first in California, and following later in Oregon and then in Washington. The estimate of -4°C temperature change from Zachos (2001) is based on the compilation and summary of data from isotopic studies of microfossils from over 40 deep sea cores over the past 10 years (Figure 1).

As geochemical tools become more precise, the causes of temperature change should be constrained. One such advance is microsampling of fish otolith growth bands

(Ivany et al., 2000; Ivany et al., 2003a) and mollusk shell growth lines (Jones 1998; Kobashi and Grossman, 2004 *in press*), which have allowed an in-depth look at the seasonal cycles of past climates. Oxygen isotope analysis of fish otoliths of the U.S. Gulf Coastal Plain have shown that a decrease in the winter low temperature leading to an increase in seasonal temperature range (from 5°C to 9°C) may have played a part in the turnover events of the Eocene-Oligocene transition. (Ivany et al., 2000; Ivany et al., 2003a).

Magnesium-Calcium Analysis

Another proxy has recently been utilized for analyzing marine paleotemperatures: magnesium-calcium ratios in carbonate skeletons (Rosenthal et al., 1997; Lear et al., 2000). The incorporation of magnesium into the carbonate matrix of shells is, in part, temperature dependent (Rosenthal et al. 1997). As temperature increases Mg is more readily substituted for Ca. The Mg/Ca system is exponentially dependant on water temperature. For every species of foraminifera the empirical relationship is slightly different. Mg/Ca ratios can be converted to temperature values using formula 3 below, which is based on studies of extant foraminifera (Rosenthal et al., 1997; Lear et al. 2002). The general formula for the Mg/Ca – temperature curve is:

$$\text{(3)} \qquad Mg/Ca = B \exp(A * BWT)$$

where A is a measure of temperature sensitivity, B is a pre-exponential constant also due to temperature sensitivity, Mg/Ca is the ratio in mmol/mol, and BWT is the bottom water temperature. A and B are different for each species of foraminifera, with A generally varying less than B across species (Lear et al., 2002). To determine A and B for each species of foraminifera, modern water temperatures are plotted against Mg/Ca concentration, and an exponential curve is fitted to the data (Rosenthal et al., 1997). The resulting equation can then be used to convert Mg/Ca data from a fossil species of foraminifera to paleotemperature, assuming the background Mg/Ca ratio of the ocean at the time being studied is known or can be estimated (Lear, 2000).

Studies have shown that Mg/Ca ratios through time have changed independently of temperature (Stanley and Hardie, 1998; Dickson, 2002). During the Phanerozoic, the oceans have had three intervals of predominantly aragonite precipitation by organisms associated with high Mg/Ca ratios, and two periods of calcite precipitation associated with high Ca concentrations and low Mg/Ca ratios (Stanley and Hardie, 1998). Estimating the secular changes through time is one of the major challenges for Mg/Ca paleothermometry. To estimate Sr flux in rivers, Lear et al. (2003) used foraminiferal Sr concentrations. Sr flux in rivers indicates the global weathering through the Cenozoic, which Lear et al. (2003) used to estimate the maximum difference between global concentrations of Sr between the past and time periods in the Cenozoic present. Changes in secular chemistry are associated with changes in mid-ocean ridge spreading rates (Stanley and Hardie, 1998). One factor affecting global levels is hydrothermal alteration of the sea floor, resulting in Mg sequestration in the rocks, which effects global Mg

levels. Higher rates of sea floor spreading lead to more alteration and thus, consumption of Mg. One possible method of precisely determining the Mg/Ca ratio of the oceans through time is by utilizing the Mg/Ca ratio of fossil echinoderms (Dickson, 2002). Comparing the Mg/Ca levels in fossils of very different ages should allow for a determination of bulk secular change. While the Mg/Ca levels in echinoderms are also temperature dependant, the secular change between ages is much larger than the change due to temperature in an individual. The curve of Mg/Ca ratios produced by this method agrees with the previous study (Stanley and Hardie, 1998), and may allow a way of calculating bulk seawater chemistry at any given time. Using bulk samples of echinoderms to get a background level should allow for paleothermometry studies to take place (Dickson, 2002).

Applications of Mg/Ca analysis

The Mg/Ca geochemical system provides a good proxy for temperature in conjunction with stable isotope analysis. At this time, the only successful tests of the accuracy of Mg/Ca in recording temperatures have been completed in tropical environments, both modern and fossil, utilizing benthic and planktonic foraminifera. (Rosenthal et al., 1997; Lear et al., 2000; Lear et al., 2002)

Several of the genera of foraminifera chosen for the current study already have Mg/Ca to temperature calibration equations determined (Lear et al., 2002). The current study attempts to use Mg/Ca ratios of both high latitude benthic foraminifera and bivalves as a qualitative comparison to oxygen isotope ratios from the same samples in

order to determine whether Mg/Ca has broader applications to paleothermometry, including separating ice signals from temperature signals in colder water samples. The importance of using the Mg/Ca system is that it is independent of ice sequestration, so an approximation of the effects of Antarctic ice formation on isotopic oxygen records can be made once the fine resolution temperature effects are separated from the secular ocean background (Lear et al., 2000). The oxygen and Mg/Ca systematics of benthic foraminifera from DSDP site 522, in the tropical South Atlantic (26°S 5°W), were compared over a span of time from the Late Cretaceous to the present to determine the effect of Antarctic ice on the oxygen isotope record (Lear et al, 2000). The Mg/Ca-temperature curve generated by Lear et al.'s (2000) study was remarkably similar to the $\delta^{18}O$ global temperature curve originally derived from Shackleton and Kennett (1975) and Miller and Fairbanks (1991). Comparing high-resolution data from the Early Oligocene oxygen and Mg/Ca records (Figure 4), Lear et al. (2000) also concluded that the positive $\delta^{18}O$ excursion in the earliest Oligocene, originally named Oi-1 by Miller et al. (1992), was most likely due to Antarctic glaciation, and not to the 5-8°C temperature change proposed initially by Miller (1992) and supported by Zachos et al. (1994) and Zachos et al. (2001).

In fact, based on the Mg/Ca data, there appears to be little change in bottom water temperatures associated with the Early Oligocene event, Oi-1 (Lear et al. 2000). While most studies still support the theory that there was significant temperature change at Oi-1, Lear et al.'s (2000) results suggest that most of the magnitude of observed isotopic

excursions is due to changing ice volume, and has very little if any mean annual temperature signal associated with it. There is additional evidence of the inception of glaciation at Oi-1 from isotopic and mineralogical variations in Australia (Mallinson et al., 2003). The Lear et al. (2000) study compared oxygen and Mg/Ca data from two separate data sets, collected at different times from different locations and environments. A side by side study of oxygen isotope data and Mg/Ca data collected at the same time may help show whether the chemical changes at the Eocene-Oligocene boundary are caused by massive ice growth, a large decrease in temperature, or some combination of the two.

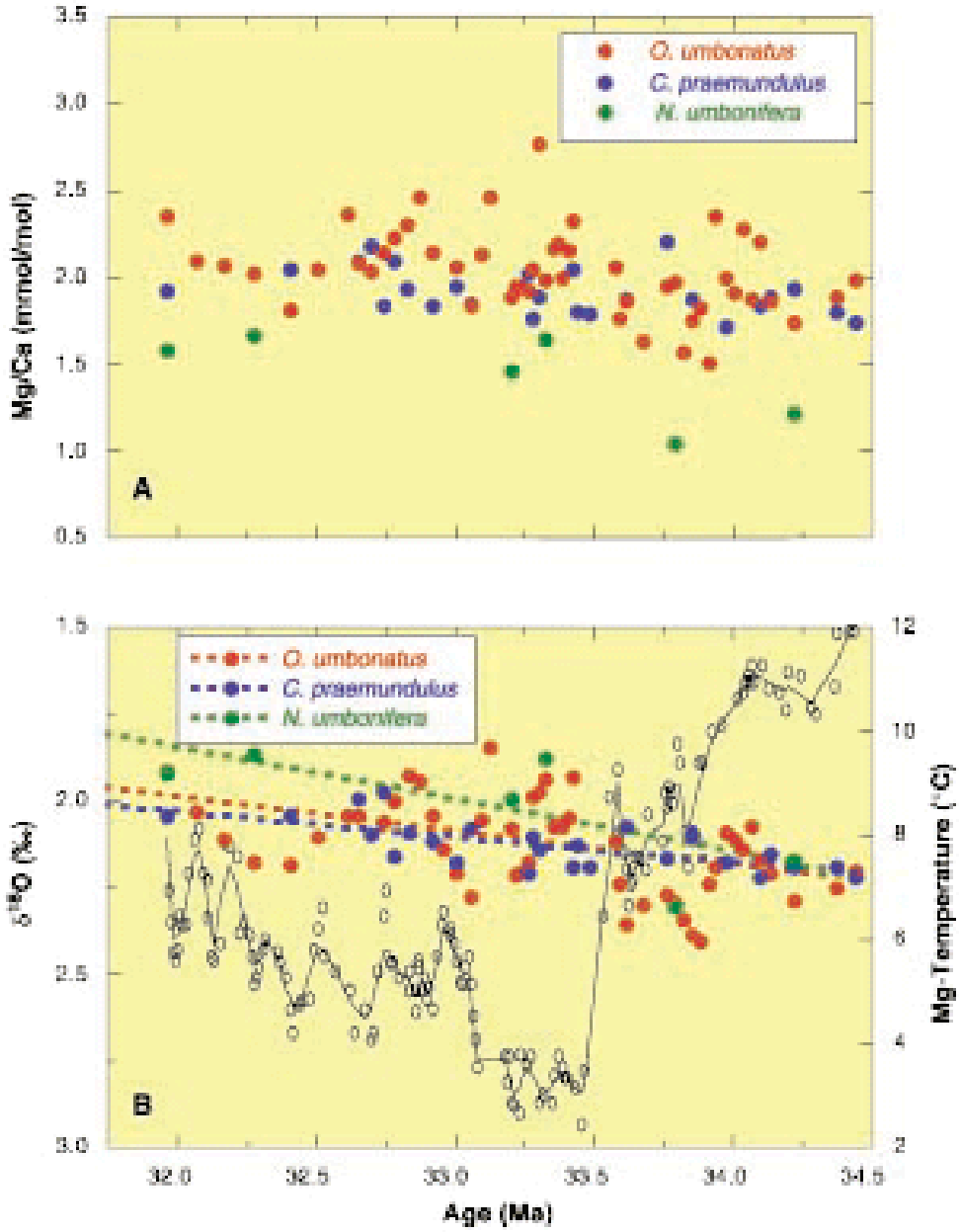


Figure 4. Mg/Ca temperature data is compared with global oxygen data (Lear et al., 2000).

Methodology

Fossil Collection

The Burke Museum provided fossils for this study from the Lincoln Creek Formation collections of J. A. Armentrout and C. P. Strong, which were supplemented by further field collecting in summer 2002 and 2003. Only those foraminiferal genera that were present in large quantities were utilized for this study, because a sample size of 8-20 individuals was needed for each technique: oxygen isotope and Mg/Ca analysis. Genera used in previous geochemical studies were also better candidates because of published calculations that account for vital effects of each taxon. Species from three genera of benthic foraminifera were chosen from the Satsop River section of the Lincoln Creek Formation, *Uvigerina, Cibicides*, and *Gyrodina*. In the Pe Ell – Doty area samples, species from *Gyrodina*, *Cassidulina*, and *Cibicides* were also selected for oxygen and Mg/Ca analysis, to maintain internal consistency in the data between genera. The bivalve *Lucinoma hannibali* was used because of its abundance in the section. *Lucinoma* is a benthic clam, which is partially dependant on chemoautotrophic symbiotic bacteria for its survival. Dando and Spiro (1993) have show for other symboint dependant bivalves that while carbon isotopes are affected by bacterial productivity, oxygen isotopic ratios are not. Stable isotopic effects for living Lucinoma have not been specifically studied.

X-Ray Diffraction

To determine whether any diagenetic alteration had occurred, and whether any secondary calcite had been precipitated, X-ray diffraction analysis was performed on

selected aragonite samples from bivalves of the genera *Lucinoma*. The foraminifera used in the study have calcite tests, and could not be tested for diagenetic effects in this way. Analysis was performed on the XRD machine at the Materials Science lab at the University of Washington. Several of the *Lucinoma* specimens were sampled, and samples were manually ground to powder and used for the test.

Sample Preparation

Bivalvia

In order to eliminate procedural artifacts from the data several different preparation procedures were used to prepare carbonate samples for analysis. *Lucinoma* shells were cleaned with distilled water, and then sampled. Samples were collected randomly from the shells of individual clams, attempting to transect as many growth bands as possible. Only the outermost layer of carbonate was collected, to get the best possible bulk average over the lifetime of the clam. Samples were collected in flakes from the umbo out to the edge. In figures 5 through 8 each data point represents a sample from a single clam. Trials 1, 2 and 3 are all taken from the same shells. For Trial 1 a Dremel drilling tool was used to remove bulk carbonate samples from the shell, however, there is evidence that isotopic alteration may occur due to the heat generated by drilling (Gill et al., 1995). Trial 2, a second complete sample set from the same fossil shells, as well as a partial third set (trial 3), used manual tools. Trial 3 was collected to reanalyze portions of the data set that were anomalous. All three sets of carbonate samples were then ground in a mortar and pestle. Samples from trials 2 and 3 were cleaned using an

oxidation/acid leach procedure recommended by Paula Rosener (pers. comm.). Samples from trial 1 were washed with distilled water, but did not undergo any chemical cleaning procedures. Comparison of the results from the sample sets show a difference between trial 1 and the other two trials (Figure 6) with almost no difference to less than 1‰ for most of the data, but with larger anomalies appearing in trials 2 and 3 at the Eocene-Oligocene boundary. Trial 3 was a partial set collected in order to determine what the actual trend of the data was in locations where the data from trials 1 and 2 differed. Trial 3 is similar to trial 2 in trend, although the absolute values are significantly different. These differences could be from differences in the bulk values of different parts of the individual bivalves. Since data points from all three trials were collected from the same bivalve, differences between individual clams cannot explain the variation in the data.

Foraminifera

Foraminifera from the Satsop sections were taken from identified collections of the Burke Museum. Tests were removed from the slides and washed with distilled water to remove any residual glue and contamination from storage. The samples were then prepared for both methods of geochemical analysis. Samples of *Cibicides* underwent the entire cleaning procedure recommended by Rosener (pers. comm.), but samples of the other two genera were only washed with distilled water and glass-distilled methanol, and not crushed or put through a weak acid leach. The samples of *Uvigerina* and *Gyrodina* were too small to go through the acid leach; the amount lost to the cleaning procedure would have made testing impossible. Comparison of the results showed some difference

in the isotopic signals, however, these differences are probably due to differing vital effects instead of cleaning procedures, since the trend of *Cibicides* and *Gyrodina* are very similar, while *Uvigerina* differs. Lear et al. (2002) showed that *Uvigerina* species tend to correlate less well (r^2 = .69) than *Cibicides* species (r^2 = .94), so differences are most likely due to vital effects between species.

Because of the small sample sizes of picked material from the Pe Ell section, those foraminifera did not undergo any strenuous cleaning, as the risk of loss was deemed too great. The sediment samples were disaggregated by soaking overnight in warm water, and sieved using a set of 80, 115 and 150 mesh-per-inch sieves. The sieved samples were then dried for approximately 20 minutes at a temperature of 80-90°C. There has been some debate over whether oven-drying samples can alter isotopic signals, however, for this study, the risk was deemed negligible, due to the relatively low drying temperatures and short times. Foraminifera were only found in the 80 mesh-per-inch seive size. The other two sieve sizes are too small to contain any of the desired genera. The foraminifera were rinsed repeatedly with glass distilled methanol and water to remove any loose clays remaining after picking.

Geochemical Analysis

The *Lucinoma* samples were run for isotopic analysis by three labs, based on instrument availability. The University of Arizona's carbonate isotope lab, under the direction of J. Cole, ran the drilled, partially cleaned samples of trial 1 for oxygen

isotopes on a Micromass Optima isotope ratio mass spectrometer equipped with an Isocarb automated carbonate preparation device. The Quaternary Research Center (QRC) at University of Washington ran the second and third sets of *Lucinoma* samples for oxygen on a Micromass Isoprime mass spectrometer similarly equipped with a dual inlet Multicarb automatic carbonate acidification device. Standards were run at the beginning and end of the run, as well as after every eighth sample. The samples were compared to the NBS19 standard, a laboratory-made equivalent to the original PDB standard. Error was calculated based on the deviation of the standards to their known isotopic value. Each trial was only run once, with no replication of samples. At the same time, a subset of the second group of shell material was dissolved in 0.15 N nitric acid and run through the Perkin-Elmer 3300 DV ICP at QRC for Mg/Ca analysis. Again, only one set was run, with no replication. Standards were run at the beginning and end of the run and compared to known values to estimate error. In both cases, oxygen and Mg/Ca analysis, the data had an error of $< 2\%$ based on deviations from the accepted standard values.

Foraminifera samples from the Satsop River section were subdivided into two groups and sent to the QRC at the University of Washington to be analyzed on either a Micromass Isoprime mass spectrometer for oxygen isotopic ratios, or on a Perkin-Elmer 3300 DV ICP for Ca, Mg, and Sr concentrations. For each analysis 10 to 20 foraminifera of the same genera were needed from each stratigraphic sample. Replicates could not be run due to the small amount of material available from each stratigraphic section. Standards were run, and error reported, in the same manner as for the bivalve runs noted

above. The oxygen analysis was compared to the NBS19 standard, and errors were again < 2%, based on deviations from the standard.

A subset of the *Gyrodina* and *Cassidulina* samples from the Pe Ell-Doty section were shipped to the University of Missouri for oxygen analysis, while the remaining *Gyrodina*, *Cassidulina*, and *Cibicides* samples were analyzed for Mg/Ca at the QRC at the University of Washington. Oxygen analysis was performed using a Finnigan MAT DeltaPlus isotope ratio mass spectrometer. Samples for Mg/Ca analysis were dissolved in 0.15N HNO_3 acid and run through a Perkin-Elmer 3300 DV ICP for Ca, Mg, and Sr concentrations.

Data Analysis

The isotopic data presented in the next section was compiled using Microsoft Excel, and presented using DeltaGraph, a statistical analysis program by Redrock software. On each graph the x-axis shows isotopic ratios for each data set. Oxygen values are relative to the PDB standard, while Mg/Ca is shown in ratios of mmol/mol. Oxygen data that trend towards the negative typically indicates an increase in temperature or a decrease in ice volume. Mg/Ca ratios are exponentially related to temperature, with an increase in the ratio indicating warming. On each graph the y-axis represents height in the section, in feet. Measurements were presented in feet for consistency because all of the previous stratigraphic work was presented in English units. The base of the section is defined for this paper as the point where the Lincoln Creek Formation first appears in the section. The sequence is unconformity-bounded at the base, and is easy to define. The

Eocene-Oligocene boundary occurs at 1800 feet and is marked for reference on the figures.

For the Satsop River sections, the stratigraphic depth of all three sections has been normalized to the Canyon River column for presentation of data. The three sections are geographically very close, and have been shown to be the same units (Rau, 1966). Based on lithological boundaries (Rau, 1966), the data sets have been combined into one. Sections were measured from one known biozonal boundary to another, and then the stratigraphic depth was normalized to that of the Canyon River section between the same biozonal boundaries. Thickness of the three sections are similar (Armentrout, 1975). This normalization and combination of the three data sets was deemed necessary to obtain a larger single data set for comparison to the global set from Zachos et al. (2001). Values on the y-axis refer to the Canyon River section. Critical points in the time scale are shown on the isotope charts to provide reference: a) the Eocene-Oligocene boundary (33.7Ma), b) the upper boundary of the benthic foraminiferal zone *Cassidulina galvinensis* and molluscan zone *Echinophoria fax* zones (31.2 Ma), and c) the Lower/Upper Zemmorian boundary (28 Ma). Oxygen isotope results include two complete trial runs of the *Lucinoma hannibali* samples (trials 1 and 2), and a third subset (trial 3) from parts of the data set with anomalous values, as well as runs of foraminifera of each genera, for both the Satsop River and Pe Ell sections. Mg/Ca data is presented from one run of *Lucinoma* carbonate, as well as from foraminifera from the Satsop River sections. For the Satsop River section, foraminiferal data from the West and Middle

Forks of the Satsop River were again normalized to the Canyon River stratigraphic column for presentation.

Results

Results of the geochemical analysis on fossils from the Lincoln Creek Formation plotted against stratigraphic depth and biozonal boundaries are presented in Figures 5-9. A compilation of all the $\delta^{18}O$ and Mg/Ca data from the foraminifera and bivalve shells is presented in Figure 5. The range in $\delta^{18}O$ obtained from bivalves through the stratigraphic section falls in the range of 0-3‰$_{PDB}$, with the exception of one negative anomaly. The range for Mg/Ca falls in the range of 0.07-0.4 mmol/mol except for an anomaly in a similar stratigraphic position. For foraminifera, $\delta^{18}O$ ranges from –1.2 to 1.9‰$_{PDB}$, and Mg/Ca ranges from 0.002 to 0.8 mmol/mol. In all of the data sets there were some values that were considered anomalous, i.e. data that fell outside of 2 standard deviations of the mean. Most notably, in both data sets there is an anomalous spike that occurs 600 ft. above the Eocene-Oligocene boundary at 33.7 Ma.

Different sampling methods on the bivalve (*Lucinoma)* shells may have had some effect on the data. Those that were sampled with the electric drill show a much smaller spike at the Eocene-Oligocene boundary (2500 ft. level). The second and third sets of analyses, performed on the same shells with samples collected manually, show a very large (-2.9 and -4.33‰$_{PDB}$) negative excursion at the Eocene-Oligocene boundary (Figure 6). However, through the rest of the data set, the three trials are fairly consistent. Only at the spike are discrepancies present. Mg/Ca and Sr/Ca measurements were performed on the second *Lucinoma* trial (trial 2) to determine if the spike was unique to the oxygen

signal. The anomaly is present only in the oxygen and Mg/Ca curves, with a very small change in the Sr/Ca curve (Figure 6). The Sr/Ca curve does not follow any trend,

Table 3. Statistical data from geochemical analysis of bivalves and foraminifera of the Satsop River sections, Lincoln Creek Formation. Temperature values were derived graphically, based on figures in Zachos et al. (2001).

Bivalve data	**$\delta^{18}O$ (trial 1)**	**$\delta^{18}O$ (trial 2)**	**$\delta^{18}O$ (all)**	**Mg/Ca**
MEAN	2.16	1.40	1.65	1.8
MEAN TEMP	1.5 °C	6 °C	5 °C	N/A
STD DEV	0.40	1.36	1.42	1.3
R^2	0.05	0.05	0.07	0.01
2 deviations	2.96-> 1.36	4.09-> -1.31	4.49-> -1.19	4.4-> -.8
R^2 (minus anomalies)	0.0009	0.0436	0.0029	0.1377

Foraminifera data	**$\delta^{18}O$ (*Cibicides*)**	**$\delta^{18}O$ (*Gyrodina*)**	**$\delta^{18}O$ (*Uvigerina*)**	**$\delta^{18}O$ (All)**
MEAN	0.46	0.41	0.93	0.46
MEAN TEMP	10 °C	10.5 °C	7.75 °C	10 °C
STD DEV	0.73	0.36	0.60	0.76
R^2	0.16	0.02	0.01	0.01
2 deviations	.929-> -1.099	1.128-> -.308	2.11-> -.25	1.95-> -1.05
R^2 (without anomalies)	0.9024			0.0011

Foraminifera Data	**Mg/Ca (*Cibicides*)**	**Mg/Ca (*Gyrodina*)**	**Mg/Ca (*Uvigerina*)**	**Mg/Ca (All)**
MEAN	2.6	2.4	2.7	2.6
STD DEV	3.0	2.2	2.2	2.4
R^2	.19	0.04	0.14	0.13
2 deviations	.84-> -.32	.68-> -0.2	.71-> -.17	.739-> -.221
R^2 (without anomalies)	0.7412			0.1767

and does not consistently correlate with the other geochemical curves generated in this study. XRD results showed that the bivalve shells used in this study were original aragonite, and that there was no new carbonate present. The XRD analysis can detect

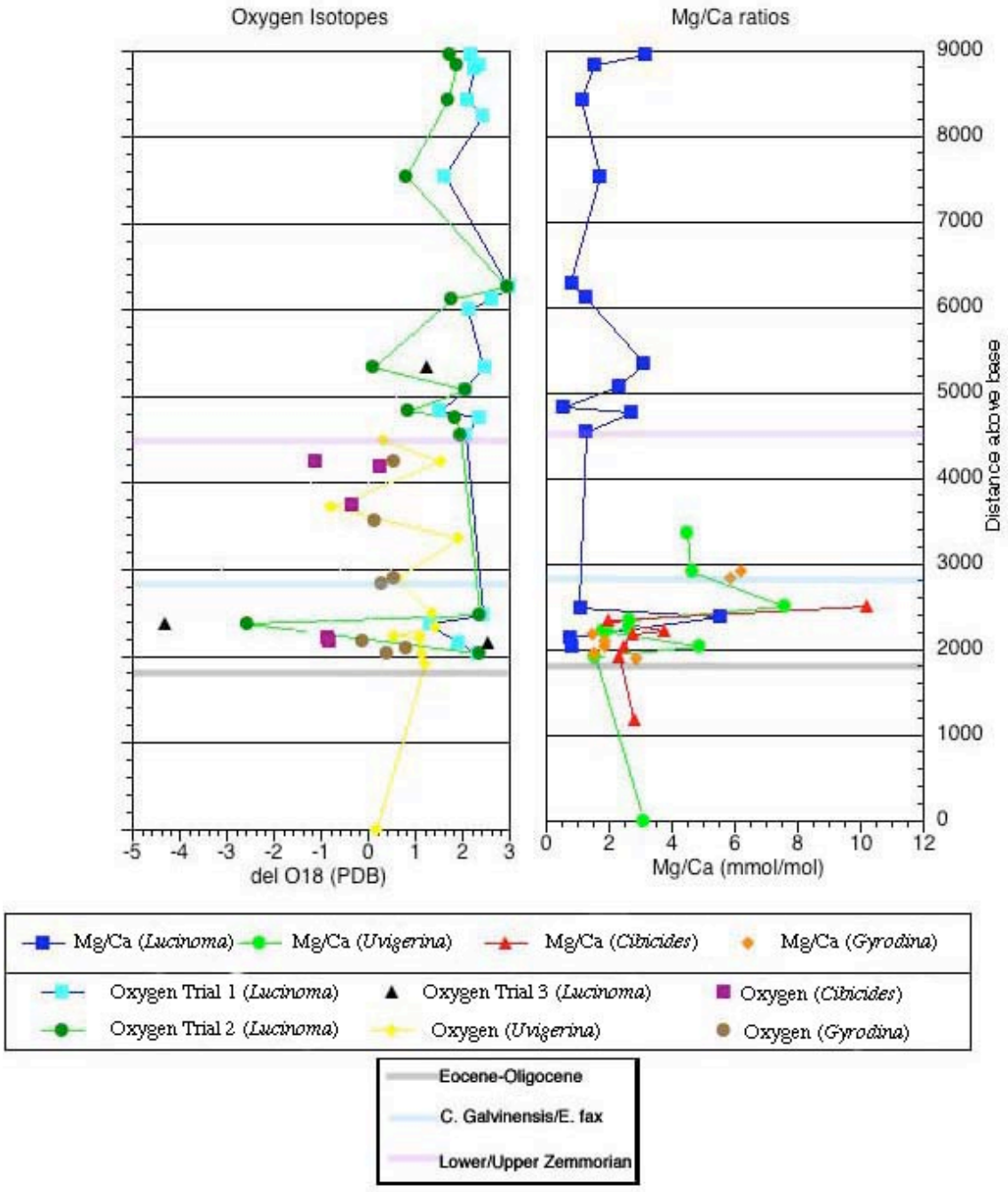


Figure 5. Comparison of all data collected from the Satsop River sections of the Lincoln Creek Formation,.

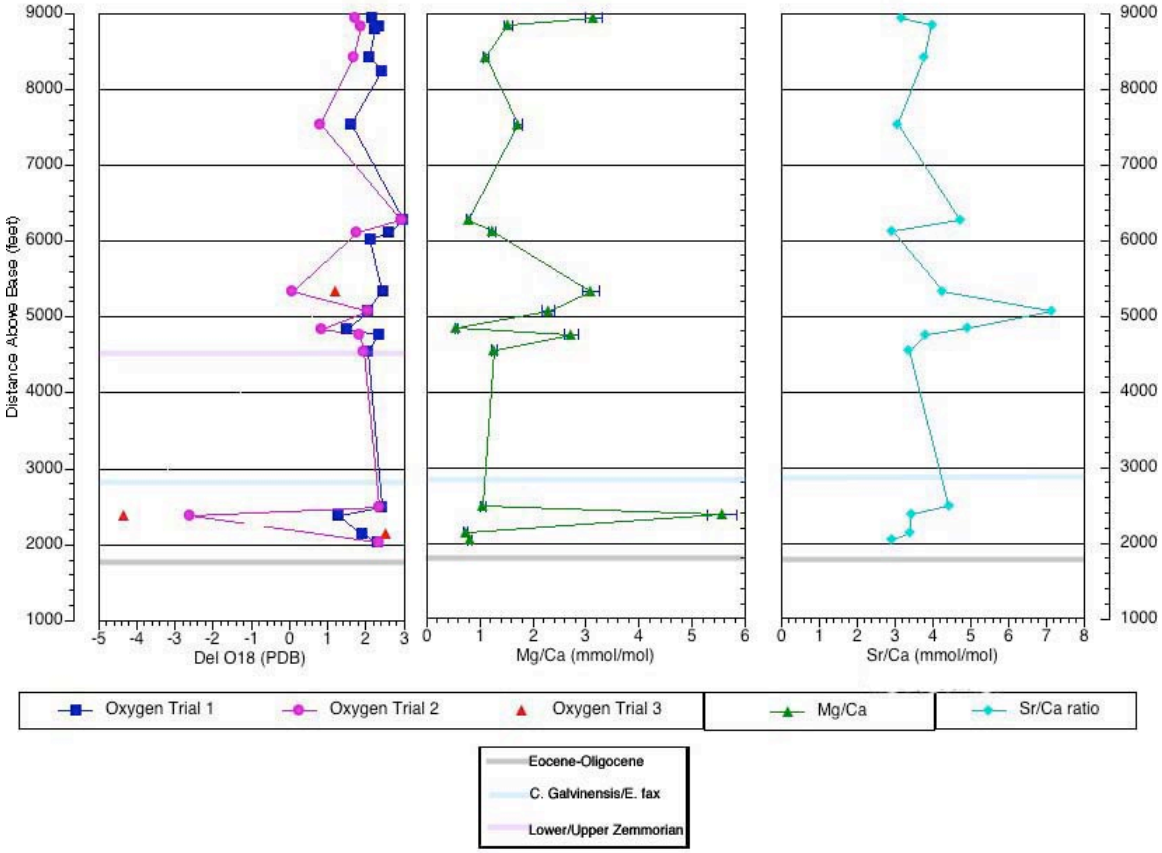


Figure 6. Oxygen, Mg/Ca and Sr/Ca data from bivalves of the Lincoln Creek Formation.

changes that effect 5% or more of the material, so there is a 95% confidence level that all of the bivalve material analyzed in this study was original.

A comparative set of analyses was obtained from species of the three selected genera of foraminifera, *Cibicides, Gyrodina* and *Uvigerina*. The Mg/Ca curve from the Satsop River foraminifera (Figure 7a) correlates well with the *Lucinoma* data set, and is within the same range, including the anomalous excursion at ~2500 feet. The foraminifera oxygen curves are offset from those of the bivalves, and do not show the large excursion present in the Mg/Ca data. Sr/Ca curves of the three genera are vastly different, and show no trend at the anomalies, as well as a very low correlation to either of the other curves (Figure 7b).

Comparison of the $\delta^{18}O$ and Mg/Ca curves of both the bivalves and the foraminifera from the Satsop River sections show that the anomalous spikes are inversely correlated across all of the trials with the exception of the foraminiferal oxygen curve (Figure 5). Foraminifera carbon isotopes only covary with oxygen in the trials using *Uvigerina* (Figure 8), and appear to be random in other trials.

Foraminiferal data from the Pe Ell – Doty section also show an internally consistent pattern between genera, with carbon and oxygen covarying (Figure 9), however, the number of data points from this section is insufficient to analyze for any quantitative temperature trends.

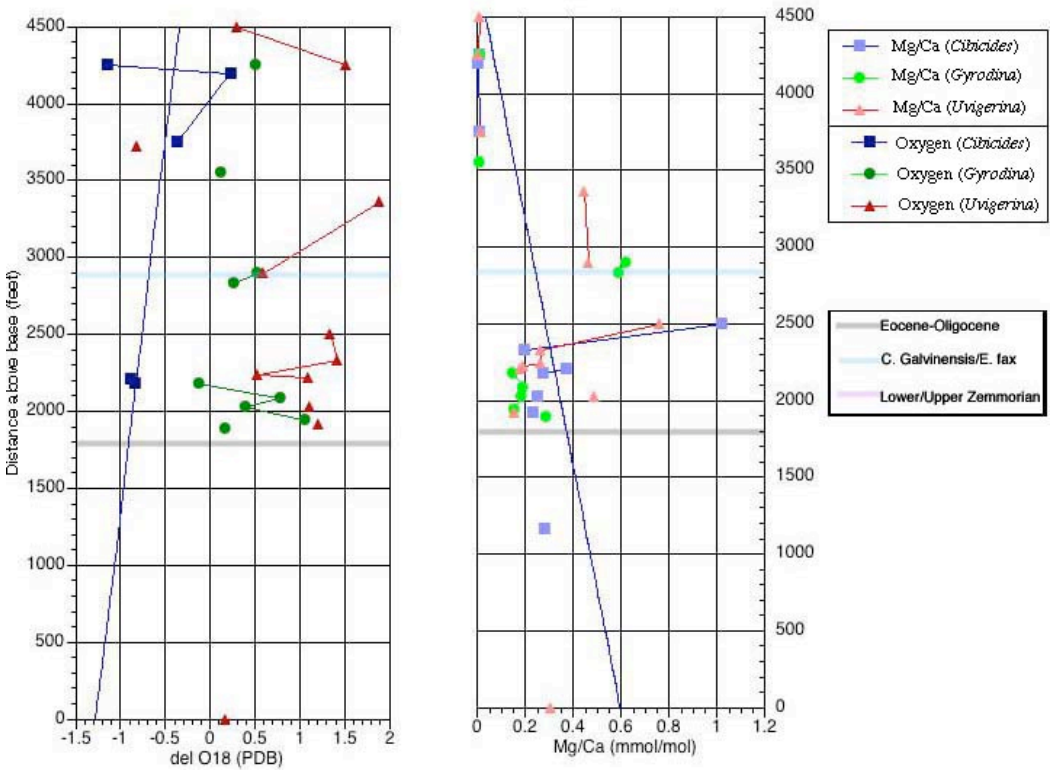
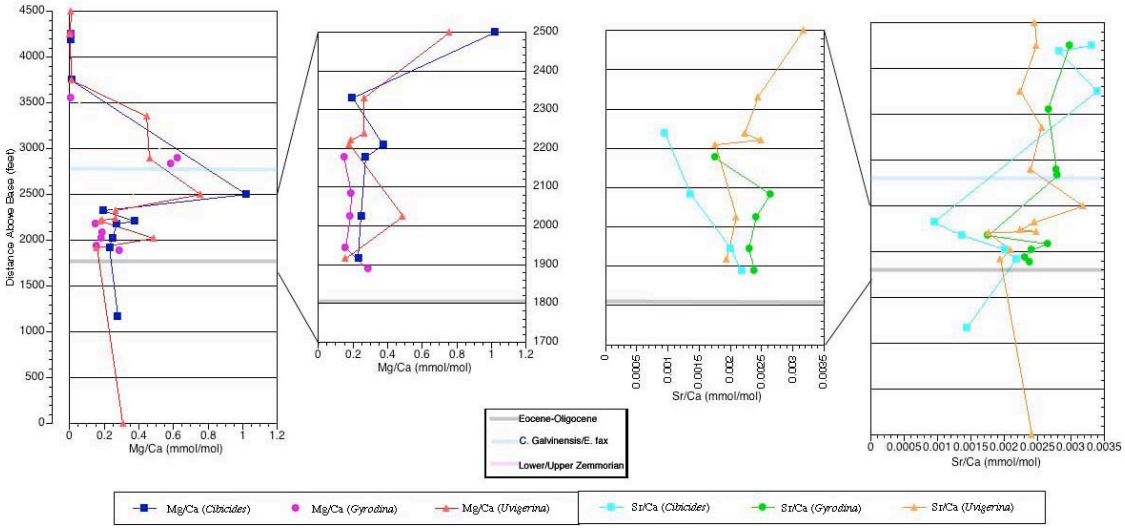


Figure 7) Data from benthic foraminifera from the Lincoln Creek Formation. a) Oxygen, Mg/Ca and Sr/Ca data comparison from foraminifera of the Satsop River sections.



b) High resolution comparison of Mg/Ca and Sr/Ca from foraminifera of the Satsop River sections with detailed diagram of 1700 – 2500 feet.

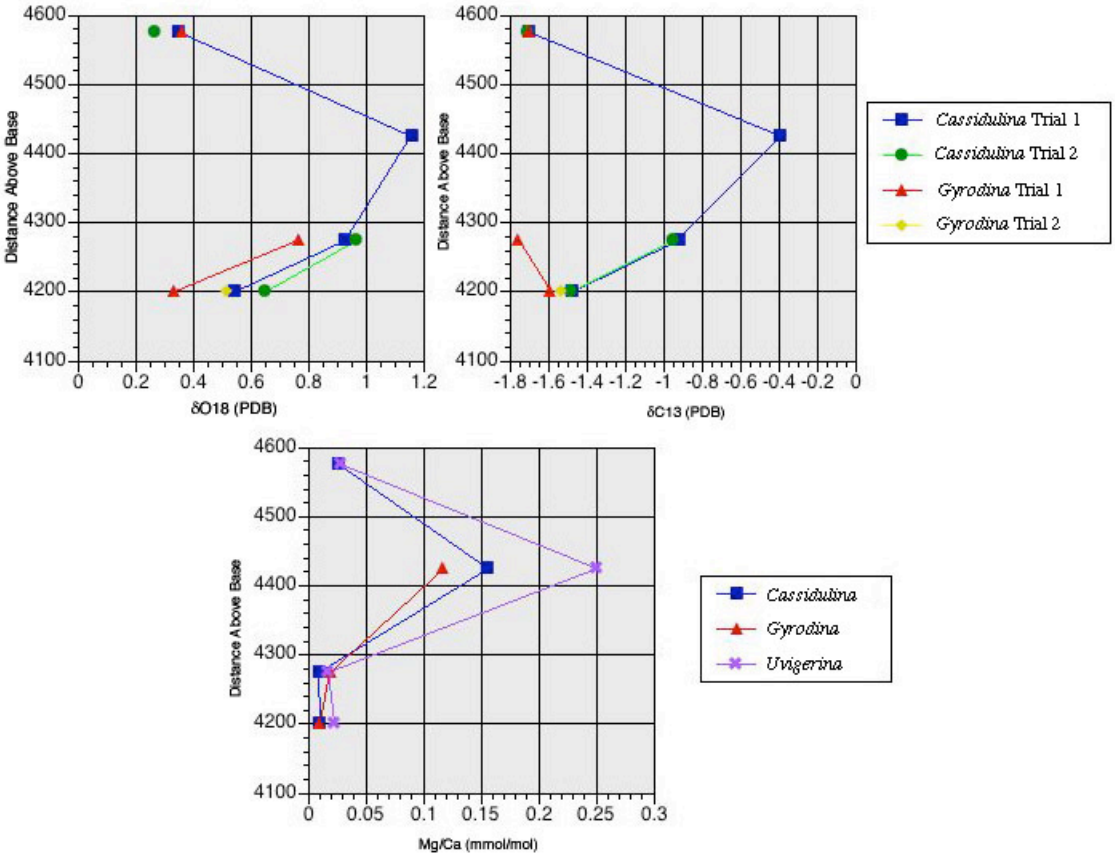


Figure 8. Oxygen, Mg/Ca and Carbon data from the Pe Ell-Doty section of the Lincoln Creek Formation.

Grain size analysis data was obtained from J. A. Armentrout's collection of Canyon River locality samples, to determine if a significant facies change could be correlated to the large negative excursion at ~2500 ft. (Figure 10). The sediment size is consistently fining upwards through the stratigraphic section, and at 1200 feet above the base of the section is a single, inconsistent stratum with an unusually high (41%) sand-sized component. However this sample was collected from a level which is considerably lower in the section than the Eocene-Oligocene boundary isotopic excursion.

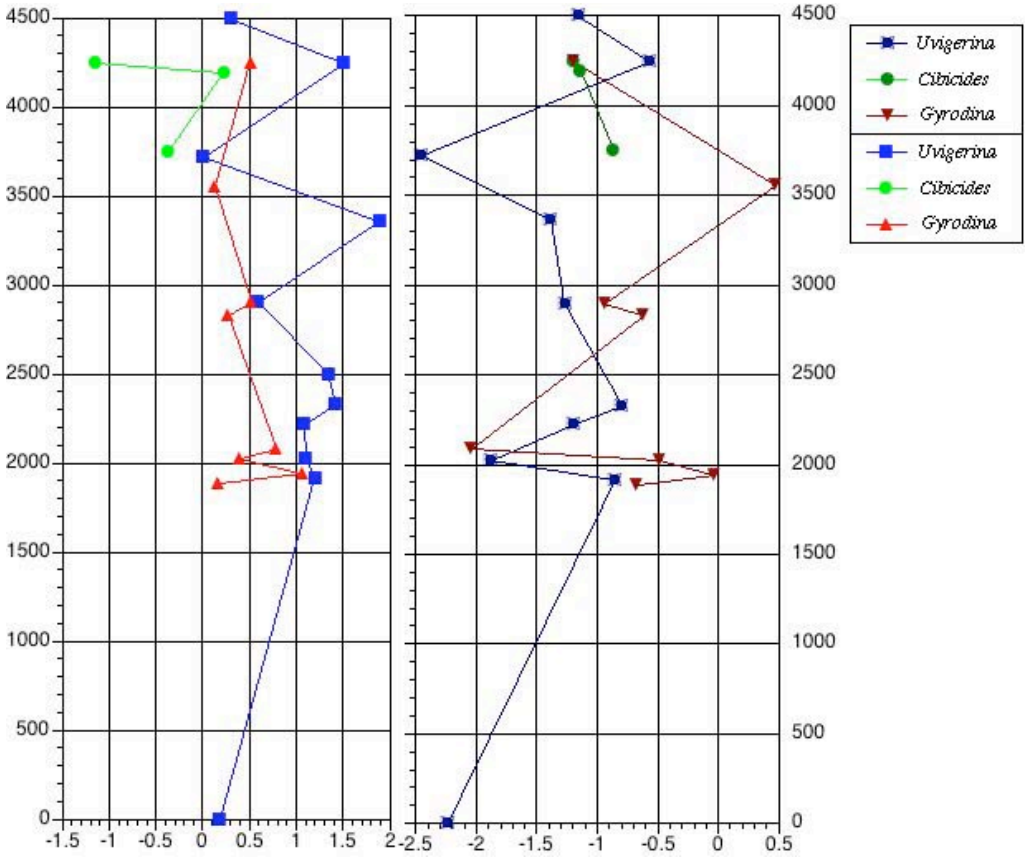


Figure 9. Comparison of oxygen and carbon isotope data from benthic foraminifera of the Satsop River sections.

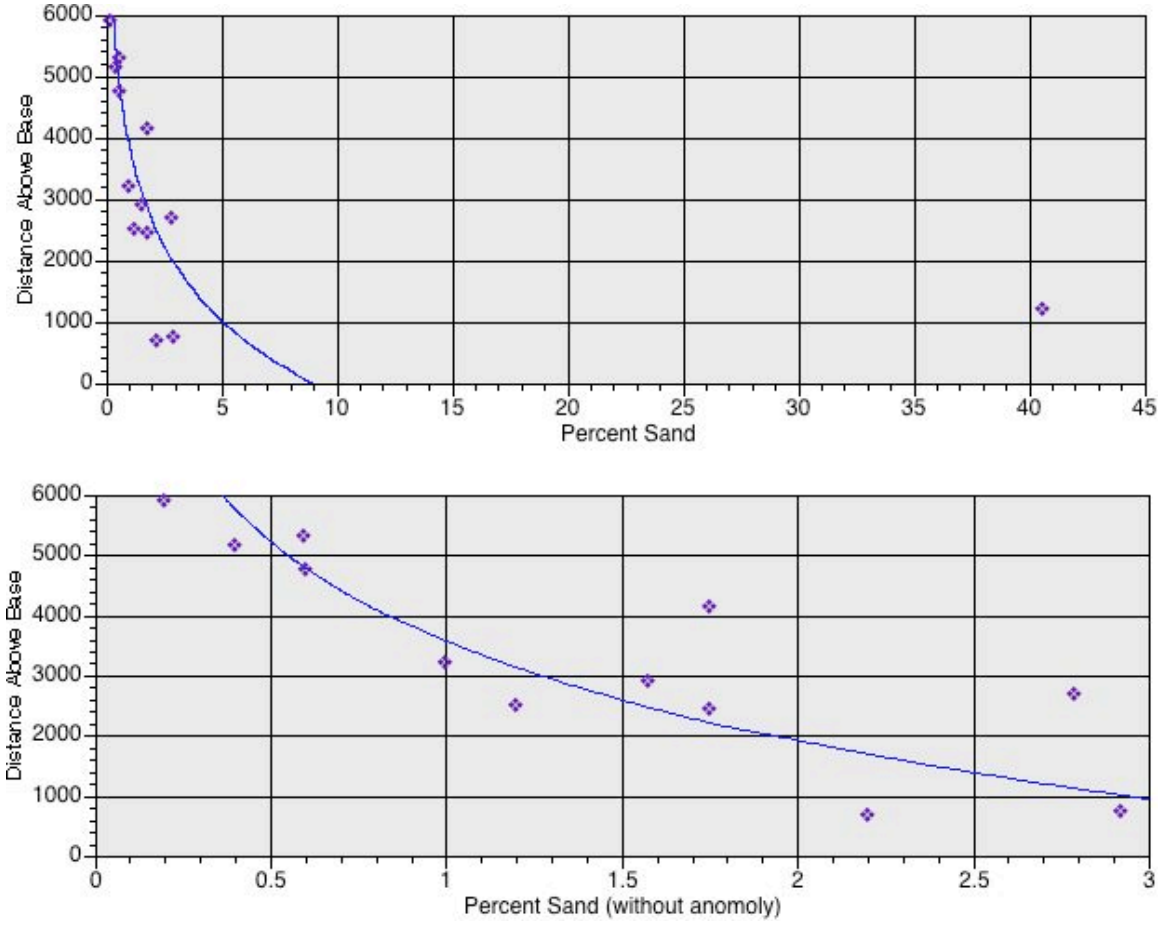


Figure 10. Grain size analysis of sediment from localities in the Canyon River section of the Lincoln Creek Formation.

Discussion

Summary of Data

The data obtained in this study provide low resolution results, but some information may still be gleaned from them. The bivalve data are more robust than the foraminifera data, since they form a larger set, and contain multiple trials. Samples of foraminifera were often at the lower limit of analytical detection for both geochemical analyses due to small sample size, and so error is expected to be higher in those trials. Oxygen isotope analysis is a more accepted measure for obtaining paleotemperature than Mg/Ca analysis, due to a much larger body of published results. In this study, the mean temperatures derived from bivalve oxygen isotopes of the Lincoln Creek Formation fauna fit in with previous DSDP results (Zachos et al., 2001). All temperatures were derived graphically based on the temperature scale shown in Figure 1 from Zachos et al. (2001). The values derived from foraminiferal oxygen isotopes of two genera are too high to concur with the presence of glendonite in the section. Mg/Ca values correlate well with oxygen, and indicate that it may be useable as a second temperature proxy. Temperature values could not be derived from mixed species data sets, however.

If the oxygen data from *Lucinoma* samples do in fact reflect paleotemperatures around the Eocene-Oligocene boundary, then they show a water temperature of anywhere from 2 to 12°C based on the temperature scale from Zachos et al. (2001). This range does not include the anomalous data present in the set, which, if reflecting temperature, would

indicate significant short term warming. In fact, the anomaly above the Eocene-Oligocene boundary is twice as large as the change from the global Eocene maximum temperature to the Oligocene minimum on the DSDP/ODP curves (Zachos et al., 2000), a change of over 20 degrees centigrade (Figure 1).

The Mg/Ca data does not yield temperature values by itself, but may give some indications as to the validity of the oxygen data. There seems is a consistent trend in the Mg/Ca curves of the three foraminiferal genera, with a uniform separation between genera, indicating that the vital effect signals have been preserved, and that alteration may not have been a controlling factor. With such a low resolution data set in terms of sampling density, and with only one sample with all three genera present, such correlations are only qualitative.

Validity of Paleotemperature Data

The low resolution and correlation of all of the data sets obtained for this study raise some questions about the presence of additional signals and error in the data, the most worrisome of these being chemical alteration of the carbonate through time. Diagenesis cannot be ruled out as a contributing factor, even though several methods were used to attempt to determine the effects before hand. XRD analysis shows no precipitation of secondary calcite for *Lucinoma*, however, if pore waters were affecting the isotopic composition of foraminifera, there would be no way to determine this through XRD.

There is an internal consistency to the data from the current study though, indicating that a meaningful trend is present. Oxygen isotope and Mg/Ca data show an inverse

relationship that is consistent through most of the study (Figures 5, 6, 7). The data from the two geochemical techniques using Lucinoma seems to be showing a constant trend. There is also a small, but fairly constant offset between the data obtained from the three genera of foraminifera for both geochemical records, indicating that perhaps even very small vital effects may have been preserved. If the samples were entirely altered, then vital effect should be drowned out by the much larger diagenetic signal. Based on all of the evidence for and against both temperature and diagenesis, there appear to be two signals in the data. It is likely that the carbonate has experienced some isotopic alteration, but is not entirely reset. While there are concerns about the resolution of the data, there appears to be some temperature signal preserved in the record. The data indicate that shallower water sections were in fact slightly warmer than the deep sea, providing an intermediate link between terrestrial and marine records.

One additional factor in the determination of diagenetic alteration is a comparison of carbon isotope ratios. In the case of the foraminifera, the $\delta 13C$ ranges from 6.6 to –2.2 (relative to PDB, see Appendix 2). The range is larger than expected for an unaltered sample, and only appears to covary with oxygen in the case of *Uvigerina*, the genus with the lowest temperature (Figure 9). Covariance is expected from samples with valid paleo-data. The absence of carbon covariance with oxygen isotope values for data from *Cibicides* and *Gyrodina*, probably indicate some alteration after deposition, while the *Uvigerina* data may be giving valid data. The carbon data is more reasonable for *Lucinoma*, but still has a high variation. However, living species of *Lucinoma* harbor chemoautotrophic bacteria in their gill tissue. Symbiont bacteria have been shown to alter

stable carbon isotopic values (Dando and Spero, 1993). In this study, little can be concluded from carbon, and the other lines of evidence for an actual temperature correlation must be believed.

If this is the case, and there is still some record of paleoclimate present, at leastfrom *Lucinoma* and *Uvigerina* data sets, then the large negative excursion must be considered significant, as it may give some indication of other processes that were occurring at the time. The excursion seen in both the oxygen and Mg/Ca curves is probably not attributable to temperature changes for the following reasons:

1) The $\delta^{18}O$ shift from 2.5‰ to –2.5‰ (or –4.33‰ in trial 3) indicates an increase in temperature of >20°C, based on published calibrations (Zachos et al., 2001). This would indicate temperatures along the northeastern Pacific margin that were higher than the Eocene maximum at ~51Ma, opposite to anywhere else in the world at this time. In contrast leaf morphology data from coastal floras of Oregon and California indicate a cooling of 2-3°C decline in average yearly temperature around the Eocene-Oligocene boundary (Kester, 2001; Myers et al., 2002; Myers, 2003).

2) The secular variation of $\delta^{18}O$ in the DSDP curve (Figure 1) shows a relatively constant temperature in the Oligocene after Oi-1, which is the first major climate shift, as defined by Miller (1992). The majority of results from Lincoln Creek Formation fauna show the same

constant paleotemperature, however, the excursion seen in the Lincoln Creek data are not present in any of the global deep sea data.

3) The presence of glendonite in the Lincoln Creek Formation also precludes high temperatures. Glendonite is a stable pseudomorph after the mineral ikaite ($CaCO_3 \bullet 6H_2O$), which forms as submarine columns and chimneys and diagenetic euhedral crystals where water temperature is in the range of –1.9°C to 7°C, with high concentration of organic carbon. The type examples are in fjords in Greenland, but glendonite is also commonly found associated with fossil cold seeps (DeLurio, 1999; Campbell et al., 2000). Glendonite is found throughout the sampled sections of the Lincoln Creek Formation, thus during deposition of the Lincoln Creek sediments temperatures at the sediment water interface could not have risen drastically, or ikaite formations could not have been present. Glendonite is found primarily in concretions in the section, and so cannot be specifically placed at the excursion, however, it does constrain the average temperature of the water.

Since the excursion is almost certainly not due to temperature fluctuations, other causes need to be considered. The next consideration is the possible effects of a rapid, short-term decrease in global ice volume. Oi-1 is characterized by an increase in permanent ice-sheets across Antarctica that extended to sea level (Zachos et al., 2000; Ivany and Van Simaeys, 2003; Kennett and Exon, 2003). Increase in global ice volume

results in a positive $\delta^{18}O$ excursion. This is in contrast to the large negative excursion shown in the Lincoln Creek data. Also, since the Mg/Ca ratios are independent of ice volume, a change in ice volume should be shown by a divergence of the oxygen and Mg/Ca curves. As can be seen in figures 5, 6, and 7, the two proxies covary inversely through the Oligocene, so neither the expected increase, nor the decrease indicated by the excursion, can be seen in the current study.

Other environmental possibilities exist for the source of the excursion, but there is no convincing evidence for any of them. Freshwater input is always a concern, however, faunal assemblages indicate an upper to middle bathyal depth (~1000 m.), on the slope. Slope deposits are deep enough that freshwater input wouldn't have as massive of an effect as the excursion seen in the data. Upwelling is another possible cause of the anomalous data point, although there is currently no other evidence indicating that a short upwelling event occurred at that time. Both changes in volcanic activity and the presence of cold methane seeps in the vicinity could have contributed to the excursions. However, neither ash layers nor cold-seep chimneys are directly associated with the samples that produced the isotopic anomalies. Grain size analysis of the Canyon River section shows that the section is fining upwards, indicating either a local transgression in this region, or a shift in sediment source during the Oligocene. There is no abrupt change in percent sand associated with the anomaly, so there is no evidence based on grain size analysis that a significant change in depositional environment caused the spikes. The most likely cause of the spike is diagenetic alteration of the oxygen and Mg/Ca data over time (Schrag et al., 1995).

While there are legitimate concerns about the validity and resolution of the data from this study, there appears to be some background temperature signal preserved in the record. If there is, then that data indicates that shelf/slope sections may have been warmer than the deep sea, and may provide an intermediate link between terrestrial and marine records.

Comparison to Global Curves

The values from the current study of $\delta^{18}O$ from the bivalves and *Uvigerina* fall within a range that is generally consistent, although slightly warmer than the global pattern for this time period, which, in the deep sea indicate temperatures of ~6°C in the late Eocene and 0 to 4°C in the Oligocene (Zachos et al., 2001). The data from the current study has very low sample density, and in all cases has a low r^2 value (from 0.15 to 0.001). However, the global DSDP/ODP curve has a lot of scatter and a low r^2, and since the data is not expected to follow a linear curve, a low regression coefficient give no indication as to the validity of the data. The global oxygen curve presented in Zachos et al. (2001) falls between 2-3‰ over the early and middle Oligocene (Figure 1), while oxygen data from this study gives values from ~0-3‰ over the same time period (Figure 6), indicating a range of anywhere from 12 to 2°C in temperature. This temperature estimate is based on the scale from Zachos (2001), and does not compensate for ice growth when producing estimated temperatures. While the data from the current study indicates warmer temperatures than the deep sea $\delta^{18}O$ curve, it is from a shallower

setting, so slightly warmer water temperatures are not entirely unlikely. Since the terrestrial data from leaf morphology of Eocene-Oligocene flora from the Pacific Northwest shows a less drastic cooling (Kester, 2001; Myers et al., 2002; Myers, 2003) than the deep ocean data, there is support for warmer water temperatures in intermediate settings. The Willamette flora of Oregon dated at 31Ma indicates considerably warmer global temperatures, based on terrestrial leaf morphology, than those predicted from the DSDP/ODP core data from the deep sea (Kester, 2001, Myers et al., 2002). Floristic data also suggest a decline in precipitation concurrent with moderate decline in temperature.

Mg/Ca data correlate well with the $\delta^{18}O$ data set (Figure 5), and are similar in values to those reported by Lear et al. (2000) over the same time span (Figure 4). Data from deep-sea cores (Lear et al., 2000) found that the Mg/Ca ratio curve did not follow the $\delta^{18}O$ curve, but instead increased constantly but slightly over the Eocene-Oligocene boundary, and into the Oligocene. The Mg/Ca curves from the current study had very low r^2, and were based on very small data sets, but again, since the accepted global trend is not linear, regression coefficients are not indicative. In the current study, the Mg/Ca curves are inversely correlated with oxygen, indicating no significant ice fluctuations, a result very different from that of Lear et al. (2000) and contrary to the current Antarctic ice-growth models. There is evidence that the large anomaly seen in the bivalve oxygen is repeated in the Mg/Ca of the bivalves and present but slightly offset in the foraminifera data sets, indicating that it is not an artificial signal, however, it is probable that the signal is linked to diagenesis.

Conclusions

The goal of this study was to use fossils from continental shelf/slope depositional environments to obtain $\delta^{18}O$ as a proxy for paleotemperature, and to make comparisons with the wealth of paleotemperature studies from deep-sea fauna. In addition, this study utilized Mg/Ca ratios from the same fossils as a way to obtain a second, independent temperature proxy. The $\delta^{18}O$ data presented in this study somewhat conforms to the published paleotemperature curves for the Eocene-Oligocene transition period, while indicating possibly warmer waters on the continental slope. The data fall near the expected range for $\delta^{18}O$ of 2-3‰$_{PDB,}$ with actual values from 0-3‰$_{PDB}$. It is also interesting to note that when anomalies are removed, there appears to be no change in temperature over the boundary, similar to conclusions reached by both leaf morphology (Kester, 2001, Myers et al., 2002) and Mg/Ca studies (Lear et al., 2000), and contrary to the deep sea records (Zachos et al., 2001). Mg/Ca was inversely correlated to oxygen, with no apparent divergence due to ice growth. Some of the discrepancies can be attributed to diagenesis of the Lincoln Creek fossils. However, this study shows the potential of performing studies on shelf and slope sections in addition to the deep sea records, in order to link the marine and terrestrial realms. The large anomalous excursion is not caused by temperature, or by any of the other obvious possibilities such as ice volume, and is another strong indicator that diagenesis has affected this data set.

This study on continental shelf/slope faunas illustrates that these geochemical analyses may provide useful temperature data. Oxygen data give values that are near the expected range, from 2 to 12°C, while the deep sea records range from 0 to 3°C (Zachos et al., 2001). This data may indicate that shallower waters trend towards the warmer temperatures observed in terrestrial studies (Kester, 2001; Myers et al., 2002; Myers, 2003). The Mg/Ca curves closely follow those of $\delta^{18}O$ indicating the Mg/Ca ratio technique is viable as a second proxy for temperature. In addition it is essential for accurately determining and removing global ice-volume effects, and determining the oxygen isotope composition of ocean water through time. The results of this study indicate that it may in fact be quite possible to use shallower water sections as an isotopic link between deep sea and terrestrial records, and that Mg/Ca is a good proxy for temperature, even in colder water settings. While the complexity of the Lincoln Creek Formation makes isotopic studies here difficult, other sections may prove less complicated, particularly sections from less geologically complicated areas, where non-temperature signals are more easily determined and corrected.

This study did contain several flaws, which should be corrected in future studies. First and foremost, more field work and collecting needs to be completed in order to more accurately constrain diagenetic effects and depth prior to geochemical analysis. Sedimentology and lithology of each sample section needs to be recorded, to look for possible indicators of depth, such as bedding structures. Also, any following studies should look for a section where depth is better constrained based on faunal assemblages,

in order to determine with certainty that the section resides in the upper mixing zone of the ocean. More testing for diagenesis needs to be performed, including cathodoluminescence (SEM) analysis, which can show secondary calcite recrystallization for all forms of carbonate, not just for aragonite like XRD analysis. Thin sections of the samples should also be made and looked at, prior to geochemical analysis, in order to look for evidence of carbonate dissolution in the sections, which would not be detected by XRD or SEM. A higher resolution section is needed, preferably with a very rapid rate of deposition, so that foraminifera can be sampled in the quantities necessary to run replicates of each data set, with localities spaced very closely together. Replicates are vital to determining the relevance of any data collected, and so it is vital to have a large sample size of foraminifera from each site. If these steps are taken at the start of the next study, many of the problems encountered here can be avoided.

More research needs to be done in all aspects of the Eocene-Oligocene transition. In particular, fossils from other shelf/slope sections form open-ocean coastlines need to be analyzed for paleotemperatures. Secondly, $\delta^{18}O$ and Mg/Ca studies need to be performed concurrently from the same samples, on high-resolution, deep-sea cores, in order to compile an accurate record of ice growth and secular changes in global oxygen. Lear et al's (2000) study is a first step, but they compared data from two different sets, which is less accurate than comparing data obtained from the same samples.

The results of this study indicate that it may in fact be quite possible to use shallower water sections as an isotopic link between deep sea and terrestrial records, and that Mg/Ca is a good proxy for temperature, even in colder water settings. While the

questions about preservation of the Lincoln Creek Formation makes isotopic studies here difficult, other sections may prove less complicated, particularly sections from a less complex region. Temperature proxies from slope and shelf sections, while more difficult to interpret than those from the deep-sea, may hold the key to reconciling differences between oceanographic and terrestrial temperature estimations at any one time period. Even though no numerical temperature data was produced from this study, it has been successful in that it does provide a springboard for additional isotopic research in shallow water sections, as well as highlight some of the pitfalls to be avoided in future studies. There are indications that further study should provide some very interesting data.

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Appendix I.

Carbonate Preparation Procedure for isotope and Mg/Ca analysis

(Adapted from the original procedure by Paula Rosener)

Kimberly Smith, 4/14/2003

I. Weighing and Crushing

Foraminifera: For the best statistics, at least 10 foraminifera were used in each sample. The total sample weight was at least 0.3mg, preferably 0.5mg. Where foraminifera were abundant enough, samples were crushed prior to cleaning, in order to clean individual chambers. If not, preparation proceeded to **Step II**. Tests were placed in the picking tray, and two glass plates or slides were prepared by cleaning them with soap and hot water, rinsing with dH_2O, and then rinsing with glass-distilled methanol. Using a small paintbrush, foraminifera tests were brushed onto one of the glass plates. The second glass plate was placed on top, and pressed down evenly just until all of the test chambers were broken open. This was verified under the microscope. Fragments from both glass plates were brushed onto a creased sheet of powdered paper, and from there, brushed into a new, dry, 14ml polypropylene or polystyrene centrifuge tube. The procedure was repeated for each sample, remembering to re-clean the glass plates in between samples.

Macrofossils: When analyzing material from macrofossils, such as bivalves, material was chipped off using a dental pick, and placed in 14ml polypropylene or polystyrene centrifuge tube, to proceed to **Step II**.

II. Removal of Fine Clays

a) A small amount of dH_2O was squirted into each tube, just enough to cover the fragments. Making sure no fragments are stuck to the walls of the tube, the rack was tapped to remove any air bubbles.

b) Tubes were placed in ultrasonic cleaner for 1-2 minutes.

c) More water was added to fill each tube tip (1mL), agitating the sample and mixing any loose clays.

d) Samples sat for 2-4 minutes, until the fragments settled. Any fragments stuck to the walls of the tubes were knocked to the bottom, then the water was siphoned off. Using a small Pasteur pipette, water was siphoned nearly to the bottom of the tube, without removing any foram fragments.

e) Steps a-d were repeated for a total of 3x's with dH_2O, 2x's with glass distilled methanol, and once more with dH_2O to rinse out the methanol.

III. Oxidizing Reagent (to remove organic matter)

a) 100 µL H_2O_2 were added to ~30mL of 0.1N NaOH in a small beaker.

b) 250 µL of the solution was pipetted into each sample and the tubes were capped.

c) The test tube rack was set into an evaporating dish, filled with dH_2O up to the bottom of the rack, on a hot plate. The water was at 80-90C (about setting 3).

d) After racks had been heating for ~5 minutes, samples were briefly ultrasonicated, then returned to the bath for another 5 minutes. Then they were ultrasonicated again.

e) More dH2O was added, being sure to rinse all fragments to the bottom. Air bubbles were removed, and samples let settle 1-2 minutes. All liquid was siphoned off and then step e was repeated. It is important to rinse out ALL of the oxidizing reagent before the next step.

IV. Sample Transfer

a) A new set of tubes was set up, with the same labels as the old set.

b) A slightly larger pipette tip was needed for this part, and was obtained by cutting off the tip of one of the plastic pipettes. The cut tip was washed in dH_2O to clean it.

c) The fragments and remaining water were siphoned up from the old tube, and expelled into the new tube. 100 µL dH_2O was added to the old tube, and transfered to the new tube with the pipette. All water was siphoned off from new tube after fragments had settled.

V. Weak Acid Leach

a) 250 µL 0.001N HNO_3 was added to each sample, it was allowed to settle* and siphoned off.

*If sample was larger, or very dirty, it was ultrasonicated for 30 seconds, and then allowed to settle.

b) After acid leaching, tubes were filled to 2 mL with dH_2O, settled, and siphoned off.

c) When all samples had been leached and rinsed, any remaining water was siphoned off, and samples were capped and stored until analysis.

d) For macrofossil samples, Samples were dried and ground in a mortar and pestle before dissolution.

e) For Oxygen Isotope analysis, the correct amount of crushed sample was transferred to the proper vial for the mass spectrometer and analyzed. **Step VI was only used for Mg/Ca analysis.**

VI. Sample Dissolution

a) 100 µL** of 0.065 HNO_3 was added to each tube and cap.

** for smaller samples 40µL of 0.065N HNO_3 was added instead.

b) If desired, tubes were placed in ultrasonic bath to speed dissolution. After about 5 minutes, bubbles were removed by rapping the tube and samples were returned to the bath.

c) After about 15 minutes, samples were checked for dissolution. If any fragments were still visible, an additional 50 µL of HNO_3 was added to the sample and it was returned to the bath.

d) Total dissolution of the sample was confirmed by checking pH. A drop of solution, was placed on a piece of 2.5-4.5 pH paper. A red spot, pH <4, indicated total dissolution.

e) If pH was high, an additional 50 µL aliquot of acid was added and the sample was tested again. This was repeated until proper pH was reached.

f) Once all samples dissolved, they were centrifuged for 5 minutes, and then run through the ICP.

Appendix II. Data from *Lucinoma hannibali* from the Satsop Sections of the Lincoln Creek Formation. Mg, Ca, and Sr values are concentration in HNO_3 solution, not actual carbonate values. Data in red are outside of two standard deviations.

Section	Genera	Locality	Dist. Above Base	$d^{18}O$	$d^{18}O$ (trial 2)	$d^{18}O$ (trial 3)	Mg (ppb) in HNO3 solution	Ca (ppm) in HN)3 soultion	Mg/Ca (mmol/mol)	Sr (ppb) in HNO3 soultion	Sr/Ca (mmol/mol)	$d^{13}C$	Litl
Canyon River	*Lucinoma*	CR 9	2040	2.32	2.34		59.00	72.59	0.81	214.00	2.95	-2.20	Siltston
Canyon River	*Lucinoma*	CR 10	2144	1.92		2.51	45.00	61.15	0.77	210.00	3.43	-1.41	Siltston
Middle Fork	*Lucinoma*	MF 5	2380	1.29	-2.60	-4.33	624.00	112.39	5.55	386.00	3.43	-2.45	Siltston
Middle Fork	*Lucinoma*	MF 6	2484	2.43	2.35		105.00	98.88	1.06	439.00	4.44	-1.32	Siltston
West Fork	*Lucinoma*	WF 10	4550	2.06	1.95		58.00	45.50	1.27	154.00	3.39	-0.52	Sandy S
Canyon River	*Lucinoma*	CR 23	4759	2.35	1.82		126.00	46.39	2.72	178.00	3.83	0.30	Siltston
Canyon River	*Lucinoma*	CR 25	4838	1.51	0.83		41.00	74.19	0.55	365.00	4.92	-2.68	Siltston
West Fork	*Lucinoma*	WF 11	5073	2.06	2.06		66.00	28.83	2.29	206.00	7.15	-5.23	Silty Sa
West Fork	*Lucinoma*	WF 12	5335	2.44	0.08	1.22	454.00	147.11	3.09	627.00	4.26	0.86	Silty Sa
West Fork	*Lucinoma*	WF 14	6015	2.11								-1.49	Silty Sa
West Fork	*Lucinoma*	WF 15	6119	2.60	1.76		89.00	71.99	1.24	210.00	2.92	-3.11	Silty Sa
West Fork	*Lucinoma*	WF 16	6276	2.96	2.92		58.00	73.25	0.79	347.00	4.73	0.24	Silty Sa
Canyon River	*Lucinoma*	CR 42	7531	1.62	0.80		188.00	109.29	1.72	336.00	3.07	-2.27	Siltston
West Fork	*Lucinoma*	WF 27	8237	2.43								-4.49	Siltston
Canyon River	*Lucinoma*	CR 50	8420	2.08	1.68		188.00	168.15	1.12	638.00	3.79	-3.12	Concret Siltston
Middle Fork	*Lucinoma*	MF 27	8786	2.24								-4.83	Siltston
Middle Fork	*Lucinoma*	MF 29	8839	2.36	1.87		175.00	113.58	1.54	453.00	3.99	-2.84	Sandy S
Middle Fork	*Lucinoma*	MF 30	8943	2.14	1.70		18.00	57.27	3.14	183.00	3.20	-3.94	Sandy S

	$d^{18}O$ (trial 1)	$d^{18}O$ (trial 2)	$d^{18}O$ (all)	Mg/Ca
MEAN	2.1619	1.3988	1.6542	1.8446
STD DEV	0.4001	1.3567	1.4239	1.3326
R2	0.0503	0.0537	0.0723	0.0016
2 devs.	2.96-> 1.36	4.09-> -1.31	4.49-> -1.19	.44-> -.08
r2 (minus anomolies)	0.0009	0.0436	0.0029	0.1377

Appendix III. Geochemical Data from *Cibicides, Gyrodina* and *Uvigerina* of the Satsop and Canyon River sections. Mg, Ca and Sr values are concentration in HNO_3 solution, not actual carbonate values.

Middle Fork	*Cibicides*	F147	2178	-0.83	16.59	6.06	2.74	8.28	1.37	5.24	concretionary silty sandstone
Middle Fork	*Cibicides*	F148	2208	-0.88	10.88	2.90	3.75			2.30	fossiliferous concretionary silty sandstone
Middle Fork	*Cibicides*	F150	2331		3.32	1.69	1.96	1.60	0.95		Massive siltstone
Middle Fork	*Cibicides*	F151	2500		14.92	1.46	10.22				tuffaceous basaltic sandstone with grit
Middle Fork	*Cibicides*	F157	4250	-1.14	0.06	10.90	0.06	0.04	3.30	-1.20	fossiliferous silty sandstone with lenses of glauconitic sandstone and conglomerate
Canyon River	*Gyrodina*	F77	1889	0.17	35.63	12.46	2.86	29.70	2.38	-0.67	silty sandstone
Canyon River	*Gyrodina*	F78	1944	1.06	18.77	12.04	1.16	27.71	2.30	-0.03	concretionary silty sandstone
Canyon River	*Gyrodina*	F80	2083	0.78	21.46	11.33	1.89	29.95	2.64	-2.04	tuffaceous concretionary silty sanstone
Canyon River	*Gyrodina*	F84	2833	0.27	111.43	18.95	5.88	52.96	2.79	-0.62	tuffaceous silty sandstone
Canyon River	*Gyrodina*	F86	3555	0.13	0.06	8.66	0.07	0.02	2.66	0.47	Massive siltstone
Middle Fork	*Gyrodina*	F146	2025	0.39	12.03	6.46	1.86	15.57	2.41	-0.48	concretionary silty sandstone
Middle Fork	*Gyrodina*	F147	2178	-0.13	11.14	7.46	1.49	13.05	1.75	6.58	concretionary silty sandstone
Middle Fork	*Gyrodina*	F153	2900	0.52	163.35	26.25	6.22	72.94	2.78	-0.94	Massive siltstone
Middle Fork	*Gyrodina*	F157	4250	0.51	0.14	17.44	0.08	0.05	2.98	-1.19	fossiliferous silty sandstone with lenses of glauconitic sandstone and conglomerate
Canyon River	*Uvigerina*	F81	2222	1.09	20.81	10.97	1.90	27.24	2.48	-1.19	tuffaceous concretionary silty sanstone
Canyon River	*Uvigerina*	F87	3722	0.01	0.05	4.03	0.02	0.01	2.23	-2.45	Massive siltstone
Canyon River	*Uvigerina*	F91	4500	0.30	0.07	7.74	0.09	0.02	2.46	-1.16	mudstone
Middle Fork	*Uvigerina*	F140	0	0.18	186.80	60.61	3.08	145.80	2.41	-2.23	basaltic fossiliferous sandstone
Middle Fork	*Uvigerina*	F145	1917	1.20	30.57	19.67	1.55	38.18	1.94	-0.85	concretionary silty sandstone
Middle Fork	*Uvigerina*	F146	2025	1.10	58.03	11.95	4.86	25.07	2.10	-1.88	concretionary silty sandstone
Middle Fork	*Uvigerina*	F148	2208		19.89	11.11	1.79	19.51	1.76		fossiliferous concretionary silty sandstone
Middle Fork	*Uvigerina*	F149	2239	0.53	37.06	13.97	2.65	31.22	2.23	1.19	fossiliferous concretionary silty sandstone
Middle Fork	*Uvigerina*	F150	2331	1.42	92.54	34.95	2.65	85.58	2.45	-0.80	Massive siltstone
Middle Fork	*Uvigerina*	F151	2500	1.34	93.28	12.29	7.59	39.10	3.18		tuffaceous basaltic sandstone with grit
Middle Fork	*Uvigerina*	F153	2900	0.59	55.22	11.94	4.62	28.57	2.39	-1.27	tuffaceous silty sandstone
Middle Fork	*Uvigerina*	F155	3361	1.89	135.75	30.39	4.47	77.73	2.56	-1.39	Massive siltstone
Middle Fork	*Uvigerina*	F157	4250	1.51	0.13	38.70	0.03	0.10	2.48	-0.56	fossiliferous silty sandstone with lenses of glauconitic sandstone and conglomerate

	$d^{18}O$ (*Cibicides*)	$d^{18}O$ (*Gyrodina*)	$d^{18}O$ (*Uvigerina*)	$d^{18}O$ (All)	Mg/Ca (*Cibicides*)	Mg/Ca (*Gyrodina*)	Mg/Ca (*Uvigerina*)	Mg/Ca (All)
MEAN	0.4507	0.4106	0.9305	0.4572	2.6480	2.3903	2.7164	2.5849
STD DEV	0.7168	0.3591	0.5949	0.7571	2.9634	2.2552	2.2245	2.4077
R2	0.1596	0.0170	0.0146	0.0088	0.1929	0.0316	0.1409	0.1242
2 deviations	.929-> -1.099	1.128-> -.308	2.11-> -.25	1.95-> -1.05	.84-> -.32	.68-> -0.2	.71-> -.17	.739-> -.221
R2 (without anomolies)	0.9024	0.0860	0.0959	0.0011	0.7412	0.1080	0.1044	0.1767

*Data points shown in red fall outside of 2 standard deviations of the mean.

Appendix IV.

Lower Lincoln Creek Formation, Middle Fork of Satsop and Canyon River sections: depth and relative temperature as indicated from benthic foraminifera assemblages.

1. Depth

Depth Assemblages are from McDougall (1980) and Ingle (1980). Some of the depth assemblages overlap.

Depth assemblages	characterized by	With the addition of
Middle neritic	*Bolivina kleinpelli* *Nonionella applini*	abundant elphidiums, lentculinids
Outer neritic to upper bathyal	*Cibicides haydoni* and *Uvigerina cocoaensis* (making up >50%)	numerous species of *Lenticulina, Guttulina, Dentalina* and *Plectofrondicularia*
Upper bathyal	numerous *U. cocoaensis, Bulimina, Globobulimina*	*Lenticulina, Dentalina, Guttulina, Plectofrondiculina, Epionides* and *Cibicides*
Middle bathyal	*Cibicides elmaensis, Valvulinariea jacksonensis V. tuneyenisis*	*Gyroidina, Cassidulina Melonis,* spinous uvigerinids, porcelaneous *Pyrula, Spiroloculina.*
Low oxygen in mid and upper bathyal	small species dominate and *Uvigerina garzaensis*	abundant Buliminacea and large costate or hispid forms of *Uvigerina.*

2. McDougall's modification of Mallory's (1959) California and Rau's (1958, 1966) Washington schemes:

2a) Stages

The late Narizian Stage:

a) *Amphimorphina jenkensi* Zone is the outer shelf to upper bathyal facies and
b) is the same ages as the *Bulimina corrugata* Zone which is middle bathyal and low oxygen

Early Refugian Stage:

a) *Cibicides haydoni* subzone = outer nertic facies and is the same age as
b) *Uvigerina atwilli* subzone = upper bathyal facies
c) *Anomalina californiensis, Sigmomorphina schencki, Uvigerina cocoaensis*

Late Refugian Stage:

a) *Uvigerina vicksburgenis* = upper bathyal
Uvigerina vickburgenis Zone is marked by the first appearance of *Uvigerina gallowayi* and *Cassidulina galvinensis*. *(U. vicksburgensis* is morphological variant of *U. cocoaensis* in a regressive sequence (Boersma, 1974). *U. gallowayi* is the. morphological variant of *U.vick* in a trangressive sequence.)

Zemorrian Stage:

a) *Buccella mansfieldi oregonensis* and *U. californica* is the base of the Zemorian Stage.

2b) Lincoln Creek Stages and Depths

Canyon River Section:

- Rau's locality F 64 -65 have abundant *Bulimina corrugata* and few *Gyroidina soldanii, Cassidulina globosa* and *Globigerina* species. late Narizian Stage, low oxygen, upper bathyal depth 200 – 600m.
- F66-73 *Gyroidina, Epionides umbonatus, Anomalina californiensis, Cassidulina globosa, Karreriella elongata*. early Refugian Stage, middle bathyal depth 600-2000m.
- F74-81 *Uvigerina garzensis, Nonion pompiloides, Gyroidina soldanii, G. orbicularis planata, Anomalina californiensis* early Refugian index species, middle bathyal depth 600-2000m.
- F82-84 *Bolivina marginata adelaidana, Gyroidina soldanii, Cassidulina galvinensis*. early Refugian Stage, upper-middle bathyal depth 200-2000m.

Middle Fork, Satsop River

- F140 *Karreriella elongata*. Earliest Refugian middle bathyal 600-2000m.
- F141-144 *Anomalina californiensis, Gyroidina soldanii*, *G. orbicularis planata, Sigmomorphina schencki, Cibicides elmaenis, Uvigerina cocoaensis* early Refugian, outer neritic- upper bathyal 100-600m.
- F145-154 *Anomalina californiensis, Bulimina alligata, Uvigerina garzaenisis Cibicides elmaenis, G. orbicularis planate, Cassidulina globosea, C. galvinensis,* early Refugian, low oxygen mid-upper bathyal zone 200-2000m.