

NORTHWESTERN UNIVERSITY

Investigation of Phosphorus Cycle Dynamics Associated With Organic Carbon Burial in
Modern (North Pacific) and Ancient (Devonian and Cretaceous) Marine Systems;
Strengths and Limitations of Sequentially Extracted (SEDEX) Phosphorus Data

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Earth and Planetary Sciences

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EVANSTON, ILLINOIS

December 2008

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ABSTRACT

Interactions Between Variations in the Marine Phosphorus Cycle and Burial of Organic Carbon –Rich Strata: Examples from the Cenomanian – Turonian Oceanic Anoxic Event 2 and the Frasnian – Famennian Biotic Crisis

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Periods of time characterized by widespread accumulation of organic carbon (C_{org}) –rich deposits have been interpreted to form as a result of increased rates of marine primary production and oxygen-deficient conditions in bottom and pore waters. Yet, debates persist regarding the source of nutrients (in particular phosphorus (P)) to marine surface waters during such intervals. In this study I attempt to address the role of P-cycle dynamics in C-burial processes using a sequential extraction procedure (SEDEX). The main focus of the study is two intervals of the geologic past characterized by widespread deposition of C_{org} –rich facies.

The first section of this dissertation (Chapter 2) explores the hypothesis that SEDEX results may be biased by post-burial diagenesis of reactive P phases. Observations spanning a range of depositional environments and geologic ages do not support this hypothesis and thus it is concluded that SEDEX provides the best available analytical approach for generating interpretable data for sedimentary P in the geologic past. The second section of this dissertation includes two chapters that examine the

role of P cycling on C_{org} burial during the Cenomanian – Turonian (C – T) Oceanic Anoxic Event (OAE) 2. Chapter 3 focuses on SEDEX results and supporting geochemical observations from a transect of sites that sample epicontinental to oceanic depositional environments. Chapter 4 describes modeling experiment designed to evaluate the roles of terrestrial input and nutrient recycling on the marine P budget during the C – T interval which provides confirmation of the hypotheses that increased terrestrial input of P could initiate OAE-like conditions while P recycling could maintain nutrient fluxes during OAE 2. An observational study of the Late Devonian was designed to assess the roles of terrestrial nutrient input versus nutrient cycling is presented in Chapter 5. The results are similar those observed for OAE 2. The final chapter (6) provides evidence of transport of authigenic phosphate minerals to marine sediments from terrestrial sources. Such observations lead to questions regarding current residence time estimates of dissolved P in the modern ocean and interpretations of C/P ratios as a productivity and redox proxy in modern and ancient marine environments.

ACKNOWLEDGMENTS

Over the last seven years I have matured as both a scientist and person in immeasurable ways. There are more people to thank for this than possible, but I would like to take a moment to mention a few.

First and foremost, my advisor, Dr. Bradley B. Sageman, has provided support in so many ways and under so many circumstances that I cannot begin to address them all. But not only would this document not be possible without him, neither would all of the wonderful things that have happened in my personal life that I have been so honored to have him be a part of.

I am also very grateful to each of my committee members: Dr. Abraham Lerman, Dr. Andrew Jacobsen, and Dr. Matthew Hurtgen. Each of these individuals has had a profound impact not only on the development of portions of this dissertation, but my growth as a scientist and educator over my tenure at this university.

The remaining faculty members of the Department of Earth and Planetary Sciences have also provided unending support whenever necessary. The open door policy of every one of them has been most appreciated and allowed me to consider each of them a friend.

Many other individuals have been instrumental in providing assistance towards the research presented here. In particular, Dr. Federica Tamburini took the time to allow me access to her lab in ETH during the summer of 2005 and train me on the SEDEX method which is the crux of this entire document. Dr. Fred Mackenzie at

SOEST was also always more than available during his visits to our department to offer an outside opinion of the research and provide invaluable assessments.

Two undergraduate students senior honors theses are a significant portion of the work presented here as well: Piyapa Dejtrakulwong and Colin Carney. I can only hope that they both learned as much from me as I did from each of them in developing their projects from start to finish.

Of course, the support of our office staff has been nothing short of amazing from the day I started here. In particular, the efforts of Mrs. Charlotte Hayes should be forever commended.

The relationships I have developed with my fellow graduate students have made every step of the way over the years here a more memorable experience. They have all provided the support both from a scientific and friendship point of view that was necessary every step of the way. In particular, my officemates Joniell Borges and Laura Swafford have become most treasured members of my new family.

Finally, nothing that I have accomplished would have been possible without the never ending love and support of my ever expanding family. They have provided me with the guidance and support always necessary throughout the trials and tribulations that come with the undertaking of this degree. And in particular, my wife, Gina, and my son, Jeremiah, whose love I share in ways that can't be put in words.

Dedicated to Grandma and Grandpa

You always wanted your grandson to be a doctor.

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CHAPTER 1

INTRODUCTION

Over geologic timescales, phosphorus (P) is believed to be the ultimate biolimiting nutrient to marine primary production, largely because its main source to the marine realm appears to be riverine input of dissolved P liberated by chemical weathering from apatite minerals in igneous and metamorphic rocks (Bjerrum and Canfield, 2002; Tyrrell, 1999). It has therefore been hypothesized that variations in the delivery of P to marine surface waters may have had a profound effect on the long term global carbon (C) cycle, and hence global climate change, throughout Earth history (Bjerrum and Canfield, 2002; Filippelli et al., 2007). In an effort to better substantiate this hypothesis, methodologies such as the SEDEX sequential extraction procedure have been developed in recent years (Anderson and Delaney, 2000; Ruttenberg, 1992) and applied in ancient marine settings (Bodin et al., 2006; Faul et al., 2003; e.g., Filippelli and Delaney, 1995; Mort et al., 2007) to identify the various P mineral phases that are preserved in ancient marine deposits. Recent work, some of which utilizes such methodologies, has demonstrated that intervals of the geologic past characterized by major perturbations in organic C (C_{org}) burial, and perhaps concomitant variations in atmospheric pCO_2 , may have been profoundly influenced by variations in the global P cycle (Bodin et al., 2006; Filippelli and Delaney, 1995; Filippelli et al., 2007; Filippelli et al., 2003; Follmi, 1995; Follmi et al., 2005; Mort et al., 2007; Murphy et al., 2000a; Murphy et al., 2000b; Nederbragt et al., 2004). However, application of the method has

also suggested an alternate hypothesis – that the riverine dissolved flux is no the only source of P that can influence production

This dissertation will further explore the alternate hypotheses for P sources and transformational processes in the marine realm. The main objective of this study is the analysis of P cycling during two intervals of the geologic past are characterized by widespread deposition of C_{org} –rich facies; the Late Devonian of the Appalachian Basin and the Cenomanian – Turonian (C – T) Oceanic Anoxic Event (OAE) 2. The strata deposited during these interpreted to have been deposited under oxygen-deficient conditions. The central methodological approach of the study is application of the SEDEX technique, but supporting evidence from other geochemical, sedimentological, and paleobiological observations will also be utilized. Questions regarding the efficiency of this methodology for analysis of ancient oxygen-deficient deposits have arisen from the observation of a linear relationship between the concentration of detrital apatite minerals and those formed authigenically in deposits from the Miocene Monterey Formation (Filippelli and Delaney, 1995). This trend was interpreted to represent post-burial diagenesis of the authigenic P (P_{auth}) minerals and therefore a misrepresentation of the occurrence of detrital P (P_{det}). Despite such possible misrepresentations of data, recent studies have continued to utilize SEDEX in Miocene (Follmi et al., 2005) and Cretaceous (Bodin et al., 2006; Faul et al., 2003; Mort et al., 2007) aged sediments without addressing whether there is evidence of such diagenesis or how it may effect the interpretations of their data. Therefore, Chapter 2 of this dissertation addresses P-phase diagenesis in ancient deposits as a pre-requisite for the Devonian and Cretaceous studies that form the bulk of this dissertation. The conclusion that utilization

of the SEDEX method is in fact appropriate for samples throughout the Phanerozoic is accompanied by an explanation of the conditions under which SEDEX results may be biased.

The following chapter provides observations and interpretations of the role of P cycling in the deposition of C_{org} -rich facies across the C - T OAE 2. Accumulation of C_{org} during this event has been interpreted as the result of increased rates of primary production and there has thus been much debate regarding the method of P delivery to marine surface waters for each. In addition to the observation based approach to OAE 2 in Chapter 3, Chapter 4 will present preliminary model results of P cycling in the North American Cretaceous Western Interior Seaway (KWIS) for the C-T interval. This study utilized previous studies of circulation in the basin to estimate river input (Slingerland et al., 1996), previously published estimates of primary production (Meyers et al., 2005), and P concentrations of modern unpolluted rivers (Meybeck, 1993) to estimate the P flux to the basin and what P burial and regeneration fluxes in deposits at the USGS #1 Portland Core Site were. Based on comparisons to the geochemical data presented in Chapter 3, the potential role of shallow epicontinental basins such as the KWIS in providing an additional source of P to the global ocean during OAE can now be evaluated.

Chapter 5 of this study will provide a similar observational approach, based primarily on data collected via utilization of the SEDEX method, as Chapter 4. This chapter is focused on the source of nutrients to the Devonian Appalachian Basin (DAB) during the Frasnian – Famennian biotic crisis. The F – F interval is also characterized

by the widespread deposition of C_{org} –rich facies interpreted to have been influenced by high rates of primary production. Also as in Chapter 3, a suite of previously published geochemical and sedimentologic data will be utilized to lend supporting evidence to interpretations of the SEDEX data.

Finally, Chapter 6 of this dissertation will provide some of the first evidence for the supply of terrestrially derived P_{auth} minerals to modern marine sediments via eolian transport. Such a flux may have a potentially significant effect on current estimates of the residence time of P in the global ocean (Ruttenberg, 2003) as P_{auth} is believed to form entirely *in situ* within sediments (Ruttenberg and Berner, 1993). It can also potentially alter interpretations of primary production and redox conditions in ancient marine environments as the utilization of the C_{org}/P_{react} ratio has been applied towards estimates of both across a broad range of modern (Anderson et al., 2001; Babu and Nath, 2005; Filippelli, 2001; Ruttenberg and Goni, 1997; Schenau and De Lange, 2001) and ancient (Bodin et al., 2006; Filippelli et al., 2007; Filippelli et al., 2003; Follmi, 1995; Follmi et al., 2005; Mort et al., 2007; Schenau et al., 2005; Slomp et al., 2002; Slomp et al., 2004) depositional environments.

In the remainder of this introductory chapter I will describe the methodologies that have been developed for sedimentary P determinations and provide justification for the choice of the SEDEX sequential extraction procedure for this study. This discussion will address application of the method to ancient depositional environments and consider some of the unique challenges involved in such studies.

Development and Advantages of the SEDEX Method

In order to understand the processes associated with the burial and diagenesis of P in marine sediments it is necessary to quantify the various solid phase P reservoirs preserved in such sediments. However, due to low concentrations of the various P phases and the fine grained nature of most marine sediment, such tasks have proven extraordinarily difficult (Ruttenberg, 1992). Utilization of direct measurement techniques, such as X-ray diffraction, require concentrations of each mineral phase greater than 1 wt. %. However, in a compilation study, Filippelli (1997) demonstrated that in modern non-phosphogenic marine sediments, total P concentrations in both open ocean and continental margin settings only range between 0.02 - 0.4 wt. %. Thus, it is necessary to utilize indirect means to quantify the various P phases preserved in most marine sedimentary deposits.

An early methodology developed by Aspila et al. (1976) was designed to separate the inorganic from the organic P fractions. Total P (P_{tot}) is determined in this method via high temperature ashing and a subsequent 1 M HCl leach of a sediment split. Inorganic P (P_{inorg}) is determined via a 1 M HCl leach of an unashed split of the same sediment sample. Organic P (P_{org}) is defined as the difference between P_{tot} and P_{inorg} . This method, now widely termed the ASPILA method, assumes that P_{inorg} represents apatite minerals from terrestrial sources that would not have been related to biologic activity prior to deposition.

Utilization of the ASPILA method in both modern and ancient marine sediments resulted in the development of the productivity – anoxia feedback (PAF) hypothesis. Based on the observation of $(C/P)_{\text{org}}$ values significantly greater than the Redfield ratio

of 106:1 (Redfield, 1958) in laminated, C_{org} – rich sediments interpreted to have been deposited under oxygen-deficient conditions, it was hypothesized that P in organic matter (OM) is preferentially removed during OM degradation under anoxic conditions. If this P was recycled to the photic zone it could drive further primary production, as well as more consumption of oxygen within the water column, thus creating a positive feedback between bottom water anoxia, enhanced nutrient regeneration, and increased rates of primary production (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Ingall et al., 1993; VanCappellen and Ingall, 1994).

The ASPILA method and concepts resulting from its utilization are based on the assumption that there is no diagenetic transformation of P other than its release in dissolved form during OM degradation. Therefore, it was assumed that all P_{inorg} measured in marine sediments is terrestrially derived and not associated with *in situ* processes in the water column or sediment. However, it was also recognized that there are solid phase P species in lakes and rivers that are associated with organic processes, but are not part of the P_{org} pool. Such phases were known to occur in association with iron oxyhydroxides and carbonate associated phosphate minerals (Lucotte and Danglejan, 1985; Williams et al., 1976). Although it was also believed that such P phases occur in shallow marine sediments as well (Filipek and Owen, 1981; Morse and Cook, 1978), quantification of such phases through indirect means proved difficult.

One of the simpler methods that has been utilized in the attempt to determine the different sedimentary P reservoirs is the correlation between P_{tot} and the elemental and

mineral chemistries of bulk sediment (Baturin, 1988; Froelich et al., 1982; Moody et al., 1988). Although this approach can produce ambiguous results (Ruttenberg, 1992), some very important early observations resulted from them. Each study demonstrated the loss of P from OM (as indicated by decreased P_{org} concentrations and increased C_{org}/P_{org} values) in the sediments across a wide range of depositional environments. Froelich et al. (1982) argued that some of this released P may become incorporated in the crystal lattice of biogenic carbonates such as coccolithophorid tests based upon the observation of increased P_{tot} concentrations in pelagic carbonates. However, a subsequent study has demonstrated that P associated with pelagic carbonates is actually associated with Fe and Mn coatings on the carbonate tests (Sherwood et al., 1987). Thus, this pathway of P removal from the ocean is not achieved via incorporation of P into the biogenic carbonate crystal lattice, but rather by the rate of formation of the Fe and Mn coatings (Sherwood et al., 1987). This conclusion has been furthered by observations of a strong correlation between Fe and Mn oxides and P_{tot} in a wide range of modern marine sedimentary environments (Baturin, 1988). It may even provide insight into the strong correlation between P_{tot} and bulk sediment accumulation (calculated on a carbonate free basis) in pelagic sediments in the central Pacific Ocean over the last 10 myr (Moody et al., 1988). Evidence indicates, however, that this is not a quantitatively significant pathway of P removal from the global ocean compared to the amount associated with burial of OM in marine sediments (Ruttenberg, 1992).

Another method used to investigate the fate of P released during OM degradation has been analysis of the pore water profiles of dissolved phosphate in shallow marine sediments (Gaudette and Lyons, 1980; Martens et al., 1978). Such

studies have demonstrated intriguing trends of decreasing pore water phosphate concentrations with depth. In clastic sediments under oxygen deficient conditions in the Long Island Sound, Martens et al. (1978) demonstrated increasing $(C/P)_{org}$ values with depth but decreasing dissolved phosphate concentrations. Through a series of stoichiometric calculations, they demonstrated that pore waters became saturated to supersaturated with respect to vivianite ($Fe_3(PO_4)_2 \cdot H_2O$) and thus hypothesized that precipitation of this authigenic phosphate mineral may be actively occurring. In a similar manner, Gaudette and Lyons (1980) demonstrated decreasing pore water phosphate concentrations with depth in shallow water carbonates off the coast of Bermuda. In their stoichiometric calculations, Gaudette and Lyons (1980) suggest that the pore waters in these sediments are supersaturated with respect to fluorapatite. Thus, they make one of the first suggestions of the diagenetic transformation of P originally deposited as OM to an inorganic apatite mineral. In each of these studies, however, there were no direct means of measuring the authigenic mineral phases that the authors suggest could be forming and thus it is feasible that more than one scenario may explain the observed trends in pore water phosphate concentrations (Ruttenberg, 1992).

The methodologies that have demonstrated the most promise for quantifying individual P phases involve various sequential extraction procedures. Such methods have been widely utilized in the study of fresh water and estuarine environments and have demonstrated a clear positive correlation between solid phase inorganic P and Fe and Mn oxyhydroxides (Lucotte and Danglejan, 1985; Williams et al., 1976) while establishing the use of a citrate dithionite – bicarbonate procedure as the more robust

method for extracting P from such Fe and Mn oxyhydroxides (Lucotte and Danglejan, 1985). Few studies prior to Ruttenberg (1992), however, had attempted to utilize such methodologies on marine sediments. Those that did (Filipek and Owen, 1981; Morse and Cook, 1978) also were able to demonstrate a clear relationship between inorganic P concentrations not associated with apatite minerals and Fe and Mn oxyhydroxides. It was also observed in such studies that there is a decrease in Fe oxyhydroxide-associated P with increasing depth in the sediment along with an increase in P concentrations that require dissolution with a stronger acid such as 1 M acetic acid (Filipek and Owen, 1981). Such observations provided some of the first evidence for P “phase switching” once the P became buried beneath the chemocline.

These early studies utilizing sequential extraction techniques, along with the ASPILA method, provided the necessary impetus for the development of the SEDEX procedure (Ruttenberg, 1992). This method consists of five extraction steps that separate the sedimentary P reservoirs into five pools: 1) loosely sorbed or exchangeable P; 2) Fe-bound P; 3) authigenic carbonate fluorapatite and other phosphatic carbonate minerals such as biogenic apatites, including fish teeth, bones, and scales (P_{auth}); 4) detrital igneous and metamorphic apatite minerals (P_{det}); and 5) P_{org} (Ruttenberg, 1992). One of the potential flaws in the sequential extraction procedure is that each of the identified P reservoirs is operationally defined. Therefore, standardization experiments were performed on each step to make SEDEX the most extensively tested P extraction procedure reported (Ruttenberg, 1992).

Each of the extraction steps within the SEDEX method are derived from preexisting procedures. Steps I – III were derived from previously developed leaching schemes for metals (Lucotte and Danglejan, 1985; Tessier et al., 1979), but modified to enhance their selectivity for P-bearing phases (Ruttenberg, 1992). Steps IV and V were derived directly from the ASPILA method. The extractants used for each step along with the phase extracted and the reactions utilized are summarized in Table 1.1. A recent study has proposed a streamlined version of SEDEX in which step I is removed (Anderson and Delaney, 2000). The justification for this is based on the assumption that phosphate will associate with Al, Fe, and other mixed oxides (Slomp et al., 1996b) and though there will be some adsorption to clays, the ionic strength of seawater results in few positive sorptive sites being available (Anderson and Delaney, 2000; Sposito, 1984). Thus, the distinction between sorbed P and oxide-associated P may be arbitrary and therefore, the four step procedure proposed by Anderson and Delaney (2000) may more accurately define both the sorbed and oxide associated fractions.

Perhaps the most significant development associated with the SEDEX method is the ability to chemically separate P_{auth} from P_{det} . This is important because P_{auth} represents deposition of a reactive P (P_{react}) phase whereas P_{det} is considered non-reactive (Ruttenberg, 1992). The P_{react} pool is interpreted as the total measurable P that might once have been bioavailable within the marine realm. The phases summed up to equal P_{react} include P associated with oxides and oxyhydroxides (P_{ox}), P_{auth} , and P_{org} (Ruttenberg and Berner, 1993).

A second significant contribution of the SEDEX method is the ability to measure the individual P phases at concentrations as low as 0.005 wt. % (Ruttenberg, 1992). As P_{tot} occurs in low concentrations in most marine sediments, this is an essential aspect of the method enables us to detect all of the individual P phases separately. Prior to the SEDEX method it was not possible to measure the occurrence of P_{ox} and P_{auth} within marine sediments and therefore it was believed that the burial of P_{org} represented the only ultimate sink of dissolved P within the marine realm (Froelich et al., 1982). However, the SEDEX method now allows for chemical analyses of these phases, as well as P_{det} and P_{org} , and therefore has led to the development of a more thorough understanding of the marine P cycle in the modern ocean (Compton et al., 2000; Delaney, 1998; Filippelli, 2002; Paytan and McLaughlin, 2007; Ruttenberg, 2003).

The most important result from the now fairly widespread use of the SEDEX method across a broad range of depositional environments has been the discovery of the *in situ* formation of P_{auth} mineral phases, in particular carbonate fluorapatite (CFA) (Anderson et al., 2001; Babu and Nath, 2005; Cha et al., 2005; Eijssink et al., 2000; Filippelli, 2001; Louchouart et al., 1997; McManus et al., 1997; Ruttenberg and Berner, 1993; Schenau et al., 2000; Schenau and De Lange, 2001; Slomp et al., 1996a; Tamburini et al., 2003b; Tamburini et al., 2002; Vink et al., 1997).

Table 1.1 – SEDEX reaction mechanisms (Ruttenberg, 1992)

Step	Extractant	Phase Extracted	Reaction
I	1 M MgCl_2 (pH 8)	Exchangeable or loosely sorbed P	Formation of MgPO_4^- complex and (or) mass action displacement by Cl^-
II	0.3 M Na_3 -citrate 1.0 M NaHCO_3 (pH 7.6) 1.125 g Na-dithionite in 45 ml of citrate bicarbonate solution	Easily reducible or reactive Fe-bound	Reduction of Fe^{3+} by dithionite and subsequent chelation by citrate
III	1 M Na-acetate buffered to pH 4 with acetic acid	CFAP + biogenic hydroxyapatite + CaCO_3 -bound	Acid dissolution at moderately low pH and (or) chelation of Ca^{2+} by acetate
IV	1 M HCl	FAP	Acid dissolution
V	Ash at 555°C 1 M HCl	Organic P	Dry oxidation at 550 °C 1 M HCl extraction of ashed residue

Such mineral phases precipitate within interstitial fluids in shallow marine sediments that become supersaturated with respect to dissolved inorganic phosphate (DIP). The DIP is sourced to such waters either directly via OM degradation within the sediment or via P released from oxides and oxyhydroxides that become reduced as the sediment crosses the chemocline (Ruttenberg and Berner, 1993; Slomp et al., 1996a; Slomp et al., 1996b). Therefore, the burial of P_{auth} mineral phases represents the ultimate sink of P originally sourced to the sediments via OM deposition. The movement of P among the different phases has been termed “phase switching” (Ruttenberg and Berner, 1993). This process is demonstrated in Figure 1.1.

Developing an understanding of the processes associated with “phase switching”, and ultimately the burial of P_{auth} mineral phases, across a wide range of depositional environments has led to revised estimates of the residence time of DIP in the modern marine realm, as well as revised interpretations of C_{org}/P molar ratios in both modern and ancient sedimentary environments. Prior to the development of the concept of “phase switching”, deposition of P_{org} was thought to be the only mechanism for permanently removing DIP from the global ocean. As P_{org} occurs in low concentrations throughout most marine sediments, the resulting calculation of the residence time of DIP was on the order of 100 kyr (Froelich et al., 1982). Most P associated with OM was believed to be released back to the marine realm during OM degradation processes. Observations also suggest that P is preferentially removed from OM (as evidenced by $C_{\text{org}}/P_{\text{org}}$ values greater than 1000) during degradation under oxygen-deficient conditions by processes such as bacterial sulfate reduction (BSR). Such observations were offered as the primary line of evidence in support of the PAF

model (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Ingall et al., 1993; VanCappellen and Ingall, 1994).

Observations from the widespread use of the SEDEX method across a broad range of depositional environments has demonstrated that much of the P released during OM degradation is, in fact, not returned to the global ocean. Rather, this P is ultimately deposited as CFA and other P_{auth} mineral phases (Fig. 1.1). Therefore, it is the formation of these P_{auth} minerals that act as the ultimate burial mechanism for DIP within the global ocean. As the burial rates of these minerals have come to be quantified across the global ocean, the residence time of DIP has been revised to the most current estimates of 10 – 17 kyr (Anderson et al., 2001; Colman, 2000; Delaney, 1998; Filippelli and Delaney, 1996; Ruttenberg, 1993; Ruttenberg, 2003).

Since the P contained within P_{auth} minerals is ultimately derived from P released during OM degradation within marine sediments, it has been suggested that these minerals must also be included in interpretations of C_{org}/P molar ratios (Anderson et al., 2001). In fact, Anderson et al. (2001) proposed that instead of calculating $C_{\text{org}}/P_{\text{org}}$ values, one should include all the P_{react} phases in such studies and instead measure $C_{\text{org}}/P_{\text{react}}$ values as this will more accurately demonstrate the release of P back to the water column vs. P burial after it is released during OM degradation. While studies utilizing this technique have demonstrated up to an order of magnitude decrease in the molar ratios compared to those calculated utilizing prior methodologies, the overall trends associated with increased P regeneration during intervals of oxygen deficiency are represented utilizing both methodologies (e.g. Carney et al., 2007, Chapter 5 of this

study). Therefore, examining the burial of P_{react} using the SEDEX method may provide the most accurate portrayal of the marine P cycle throughout Earth history.

Utilization of SEDEX Within Ancient Marine Sediments

Whereas the SEDEX method has been extensively utilized in a wide variety of modern marine environments, its application to ancient marine strata has been comparatively limited to date. The most extensive application of this method to ancient marine deposits has involved the formation of Mediterranean sapropels (Filippelli et al., 2003; Slomp et al., 2002; Slomp et al., 2004). These C_{org} – rich deposits have been interpreted as the result of combined increase in rates of primary production and enhanced conditions for the preservation of OM (Calvert et al., 1992; Passier et al., 1999; Rohling, 1994; Slomp et al., 2002; Thomson et al., 1999). Since the Mediterranean is currently a P limited system, the mechanisms for delivery of P to surface waters (in order to initiate and maintain the interpreted increases in primary production during sapropel deposition) has been a subject of keen interest. Climate induced increases in continental runoff have been proposed as a possible explanation for the initiation of such conditions (Hilgen, 1991; Rossignolstrick et al., 1982). However, an alternative hypothesis suggests a PAF-type model for maintaining increased rates of production during periods of sapropel deposition.

The Mediterranean sapropels are interpreted to have been deposited under sulfate reducing conditions in marine bottom and pore waters. Therefore, one would

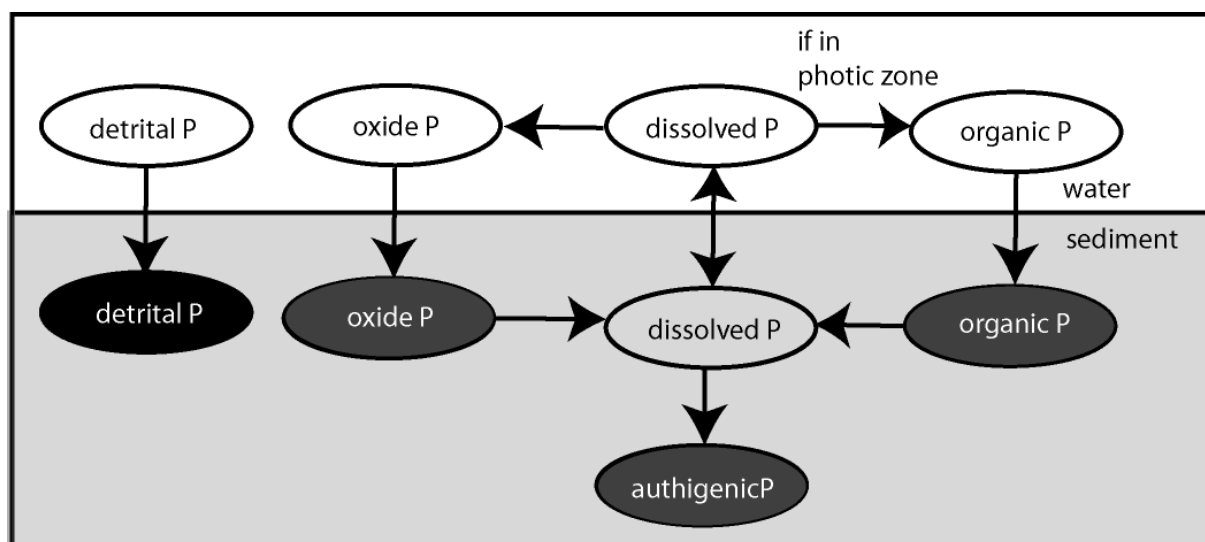


Figure 1.1. Schematic demonstrating the relationship between the various measured P phases utilizing the SEDEX method. P_{react} is the sum of the oxide, organic, and authigenic P fractions. The movement of the P between these phases represents the process of “phase switching”. Detrital P is considered non-reactive and is interpreted to represent deposition of igneous and metamorphic apatite minerals derived from terrestrial input. Adapted from Filippelli and Delaney (1996).

expect such deposits to demonstrate elevated C_{org}/P_{react} values, as well as a decreased burial efficiency of P_{react} . This prediction has been tested and verified with samples spanning a wide spatial and temporal realm throughout the Mediterranean (Eijssink et al., 1997; Filippelli et al., 2003; Slomp et al., 2002; Slomp et al., 2004). In each of these studies, elevated C_{org}/P_{react} values along with decreased burial efficiencies of P_{react} were identified in C_{org} -rich deposits showing other evidence for accumulation under oxygen-deficient conditions. Thus, in the study of Mediterranean sapropels, SEDEX has provided strong evidence for the PAF model as a mechanism associated with deposition of ancient C_{org} -rich strata.

Further application of the SEDEX method in ancient marine deposits has focused upon strata of the Miocene Monterey Formation (Filippelli and Delaney, 1995; Föllmi et al., 2005), pelagic deposits of the Late Cretaceous through early Paleocene (Faul et al., 2003), Oceanic Anoxic Event 2 (Mort et al., 2007), and the Late Hauterivian Oceanic Anoxic Event (Bodin et al., 2006). In each of these studies, variations in the marine P cycle, as interpreted from observations of P_{react} species, were linked to changes in redox conditions in bottom and pore waters and/or productivity rates during an interval of significant global climatic change. However, because of interpretations of potential post-burial diagenesis of P_{auth} mineral phases (Filippelli and Delaney, 1995), such studies have been unable to utilize accumulation of P_{det} mineral phases as any sort of proxy for detrital input. After addressing this concern, this dissertation will expand the utilization of the SEDEX method to more accurately determine the role of P cycling during OAE 2, as well as apply this method to the Late Devonian F-F extinction event.

CHAPTER 2

POTENTIAL DIAGENESIS OF AUTHIGENIC PHOSPHATE MINERALS OVER GEOLOGIC TIMESCALES: IMPLICATIONS FOR INTERPRETATIONS OF THE MARINE PHOSPHORUS CYCLE IN THE GEOLOGIC PAST

2.1 INTRODUCTION

A common conclusion of studies seeking to understand the widespread deposition of organic-carbon (C_{org}) rich facies during intervals of the geologic past is that increased rates of marine primary production played an important role (Arthur et al., 1988; Arthur et al., 1987; Dumitrescu and Brassell, 2006; Hochuli et al., 1999; Kuypers et al., 2002; Meyers, 2006; Pedersen and Calvert, 1990; Sageman et al., 2003). However, there is still much debate regarding the source of nutrients that would have been necessary to support increased rates of primary production. Some studies have begun to address the role that phosphorus (P) may have had on such intervals (Bjerrum et al., 2006; Handoh and Lenton, 2003; Mort et al., 2007; Murphy et al., 2000a; Nederbragt et al., 2004) based on the assumption that P acts as the ultimate biolimiting nutrient on marine primary production over geologic timescales (Bjerrum and Canfield, 2002; Tyrrell, 1999). This assumption stems from the knowledge that unlike carbon (C) and nitrogen (N), the ultimate source of P is constrained to the flux from chemical weathering of igneous, metamorphic, and sedimentary rocks.

Development of sequential extraction procedures such as the SEDEX method (Anderson and Delaney, 2000; Ruttenberg, 1992) now make it possible to differentiate the four P-bearing phases deposited in marine sediments. These phases include P

sorbed to oxides and oxyhydroxides (P_{ox}), authigenic apatite minerals (P_{auth}), detrital apatite minerals (P_{det}), and P in remnant organic matter (P_{org}). The interaction between these phases in the water column and shallow marine sediments is demonstrated in Figure 1.1. These phases can be divided into two categories: reactive (P_{react}) and nonreactive. The P_{react} value can be obtained from the sum of the P_{ox} , P_{auth} , and P_{org} phases and is defined by each phase containing P from a reservoir that at one point may have been bioavailable. Nonreactive P is defined as the concentration of P_{det} and it is assumed that the P in these minerals was never available for primary production.

Perhaps the most important contribution that utilization of the SEDEX method has made is the ability to distinguish P_{auth} from P_{det} . Although it was widely recognized that P_{auth} minerals become concentrated along upwelling margins in modern and ancient marine environments, prior to development of the SEDEX method available petrographic and chemical techniques were not able to distinguish these minerals from P_{det} phases. In developing SEDEX, Ruttenger (1992) recognized that because P_{auth} minerals contain CO_3^{2-} substituting for PO_4^{2-} in the apatite crystal lattice, such minerals are more soluble than P_{det} mineral phases. Therefore, P_{auth} minerals can be dissolved utilizing a weaker acid than P_{det} minerals.

A major discovery made through utilization of the SEDEX method has been the recognition of *in situ* formation of P_{auth} minerals along non-upwelling continental margins (Ruttenger and Berner, 1993). This discovery has since been verified in marine sediments across a wide range of depositional environments (Babu and Nath, 2005; Cha et al., 2005; Eijsink et al., 2000; Filippelli, 2001; Schenau et al., 2000; Schenau and

De Lange, 2001; Slomp et al., 1998; Tamburini et al., 2003a; Tamburini et al., 2003b; Vink et al., 1997; Virtasalo et al., 2005). Such discoveries have led to a fundamental change in our understanding of the marine P cycle. Most significant to studies of ancient marine settings is the understanding that P_{react} concentrations must be considered rather than P_{org} when utilizing variations in C/P molar ratios as a redox and paleoproductivity proxy (Anderson et al., 2001).

Studies utilizing SEDEX in ancient marine deposits have demonstrated that the vast majority of P_{react} is preserved as P_{auth} mineral phases (Anderson et al., 2001; Bodin et al., 2006; Faul et al., 2003; Filippelli and Delaney, 1995; Filippelli et al., 2003; Follmi et al., 2005; Mort et al., 2007). This has led to the interpretation that P_{auth} minerals are the ultimate sink for P released during organic matter (OM) degradation (Fig. 1.1). However, it has also been suggested that over geologic timescales, there may be further diagenetic alteration of P_{auth} minerals that ultimately make them less soluble such that they chemically resemble P_{det} minerals. This was first hypothesized in a study of the crystallinity index values of P_{auth} minerals in the Monterey Formation (Shemesh, 1990). In his study, Shemesh (1990) demonstrated that higher crystallinity indices correlated to P minerals with lower carbonate contents. This was explained by the fact that biogenic apatites except tooth enamel are poorly crystallized and therefore, well-crystallized biogenic apatites must have been the result of recrystallization during diagenesis (Puceat et al., 2004; Shemesh, 1990; StuartWilliams et al., 1996). Samples with high crystallinity indices also showed a positive correlation to diagenetic indicators such as $\delta^{18}\text{O}$ and rare earth element (REE) concentrations. Shemesh (1990) therefore concluded that P minerals with high crystallinity indices must have been diagenetically

altered post burial in a process that involved the loss of their carbonate content. Such diagenetic alteration was termed decarboxylation.

A subsequent study utilized the SEDEX method on samples of the Miocene Monterey Formation and discovered a trend of increasing P_{react} with increasing P_{det} concentrations (Figure 2.1) in an interval of phosphatic black shales (Filippelli and Delaney, 1995). Decarboxylation was proposed as a possible mechanism to explain this trend. Later studies of the same formation verified this trend and also invoked the decarboxylation mechanism to explain the occurrence of P_{det} in deposits from a hemipelagic marine environment containing no other indicators of significant terrestrial input (Follmi et al., 2005). Another study recently employed similar observations to discount P_{det} accumulation in strata spanning the Cenomanian – Turonian (C-T) Oceanic Anoxic Event (OAE) 2 across a wide range of depositional environments (Mort et al., 2007). The authors concluded that increased primary production associated with OAE 2 was caused by an increased nutrient flux to marine surface waters resulting solely from enhanced recycling of P from decomposing OM under oxygen deficient conditions.

A need to re-examine the assumptions on which the decarboxylation hypothesis is based has been suggested by recent analysis of the crystallinity index methods of Shemesh (1990). Pucéat et al. (2004) utilized a Raman spectroscopic, technique which more efficiently determines the crystallinity indices of biogenic apatites, over a selection of samples spanning the entire Phanerozoic and demonstrated that crystallinity index is, in fact, a poor proxy for potential diagenetic alteration. This result prompts a more

detailed assessment of the Filippelli and Delaney (1995) hypothesis that diagenetic alteration of P_{auth} to more insoluble mineral phases may bias results from the SEDEX method. In order to complete this assessment SEDEX results from samples of ancient marine strata spanning a wide range of geologic ages and depositional environments. Samples are examined from three cores: 1) the USGS #1 Portland core spanning the C-T OAE 2 interval and representing deposition in a shallow marine epicontinental seaway (Fig. 2.2); 2) ODP Site 1258 spanning the C-T OAE 2 interval and representing deposition in a hemipelagic – pelagic marine environment at middle – upper bathyal water depths (Fig. 2.2); and 3) the NX-1 West Valley Core representing deposition spanning the Frasnian – Famenian (F-F) boundary and concomitant biotic crisis in deposits of a shallow epicontinental marine setting (Fig. 2.3). The selection of these sites allows for the assessment of potential P_{auth} diagenesis across a wide range of depositional environments and geologic ages. Each of the sites chosen also has significant volumes of previously published sedimentologic and geochemical data (Erbacher et al., 2005; Erbacher et al., 2004; Murphy et al., 2000a; Sageman et al., 2003; Sageman et al., 1997; Sageman et al., 1998) for further evaluation of the mechanisms causing the observed P data in this study. Trends in the relationship between P_{react} and P_{det} measured in this study will be compared to those of Filippelli and Delaney (1995) to help address the hypothesis that rates of P_{det} accumulation in ancient marine settings provide a relative proxy for terrestrially derived fluxes of dissolved P to the marine realm.

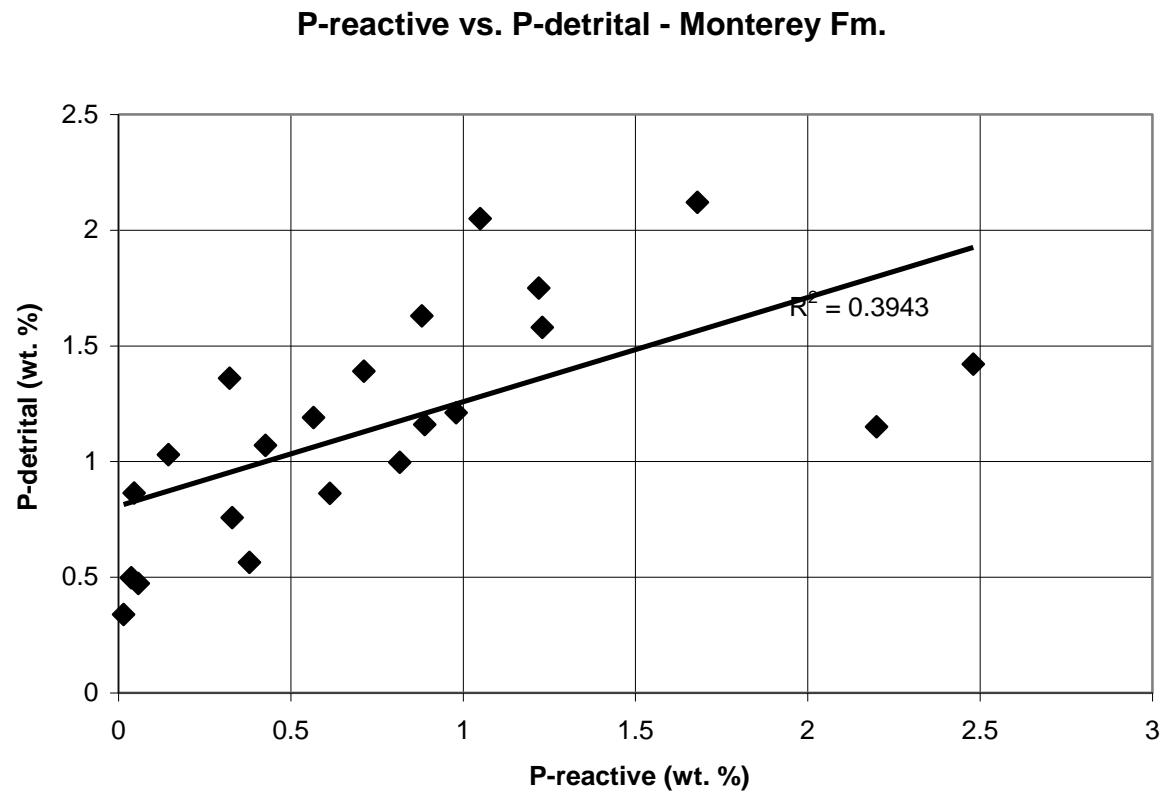


Figure 2.1. Cross plot of P_{react} vs. P_{det} from the phosphatic shales of the Monterey Fm. (Filippelli and Delaney, 1995). The linear trend of increasing P_{det} with increasing P_{react} demonstrated in this plot has been interpreted as supporting evidence for the decarboxylation hypothesis (Shemesh, 1990).

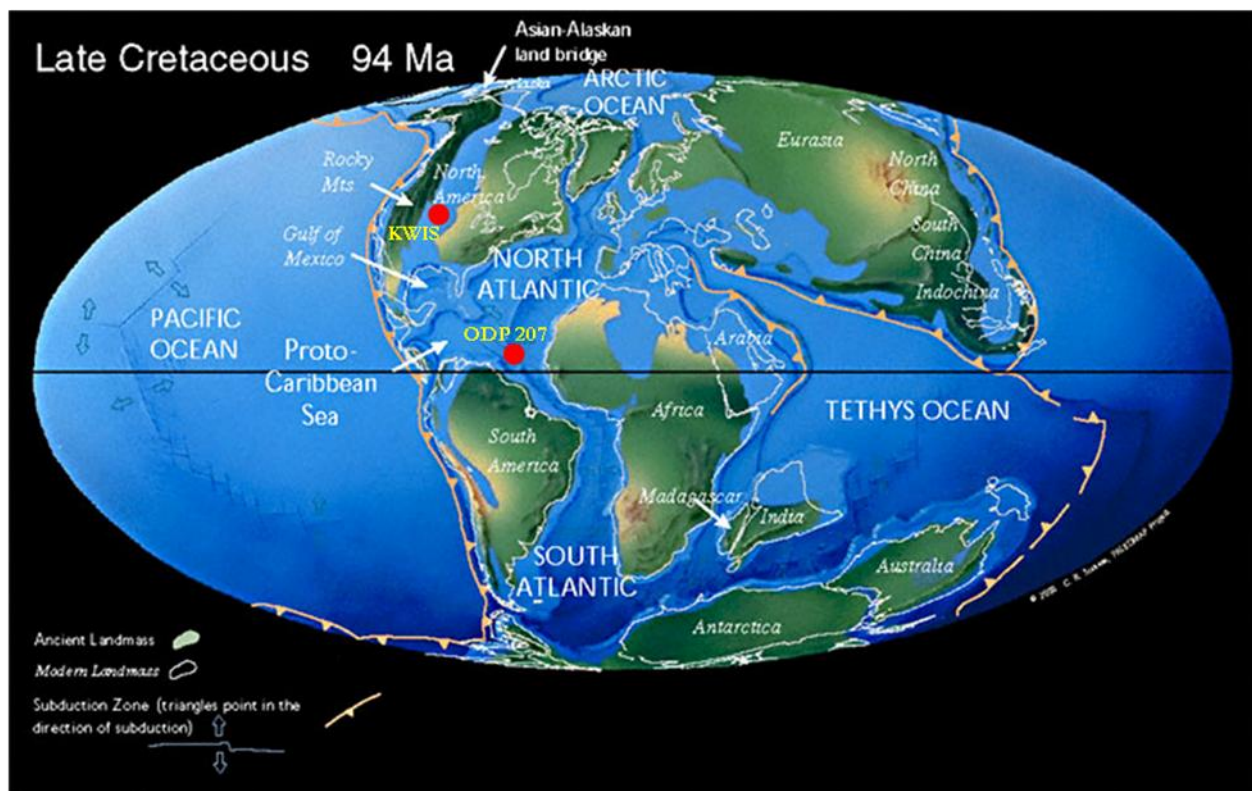


Figure 2.2. Late Cretaceous paleogeographic map with locations of ODP Leg 207 and the USGS #1 Portland Core. Adapted from www.scotese.com

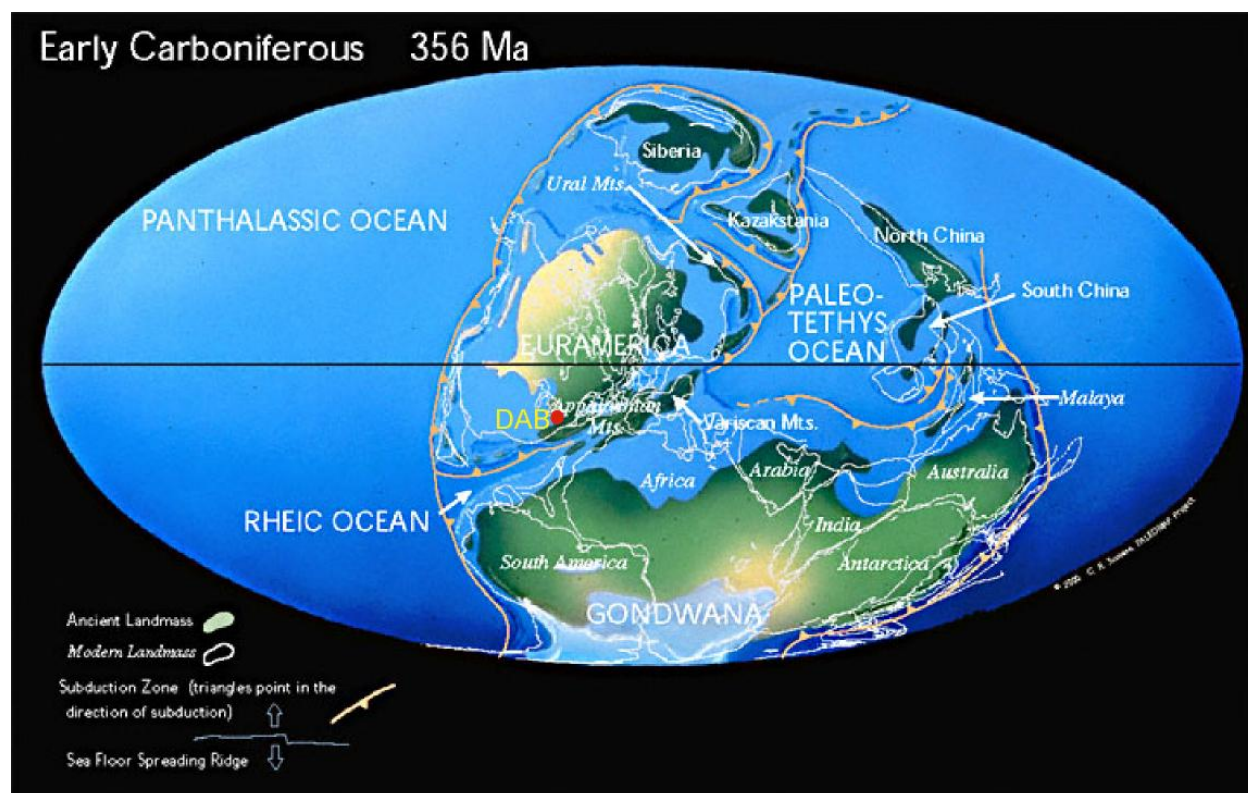


Figure 2.3. Paleogeographic map of the Devonian Appalachian Basin during the Early Carboniferous (approximately 8 myr following the F-F boundary) with the locale of the West Valley Core. Adapted from www.scotese.com

2.2 METHODS

The SEDEX method (Ruttenberg, 1992) was applied to powdered rock samples crushed to 200 mesh. Step 1 of the procedure (measuring the concentration of exchangeable P) was omitted based on the observation across a wide range of modern and ancient depositional environments, that such concentrations are very low (Anderson and Delaney, 2000). Therefore, the first step in studies utilizing this streamlined procedure measures both the exchangeable and iron-oxide bound (Fe-P) species. The remaining P species include authigenic apatite minerals (P_{auth}), detrital apatite minerals (P_{det}), and P in remnant organic matter (P_{org}). The extraction procedure for each phase is summarized in Table 1.1.

Concentrations for each species were measured using standard spectrophotometric techniques on a Shimadzu UV-1601 UV-visible spectrophotometer. Color development for each extractant was achieved utilizing standard molybdate blue methodologies (Strickland and Parsons, 1972). Relative errors for each of the SEDEX steps in this study are 10.2%, 1.1%, 3.5%, and 9.8% respectively. Since P_{ox} and P_{org} concentrations are generally less than 2 $\mu\text{mol/g}$, the larger errors associated with these phases are not significant.

2.3 RESULTS AND DISCUSSION

2.3.1 EPICONTINENTAL MARINE SETTINGS

Due to their proximity to uplifted mountain belts that supplied massive volumes of sediment, which ultimately filled the Cretaceous Western Interior Seaway (KWIS) and Devonian Appalachian Basin (DAB), these sites should record detrital signals if they are present. Cross plots of P_{react} versus P_{det} of samples from both the West Valley Core spanning the F-F boundary (Fig. 2.4) and the Portland Core spanning the C-T OAE 2 (Figure 2.5) vaguely suggest that the maximum P_{react} values are associated with decreased P_{det} concentrations, but the data are clearly non-linear. Samples from these cores span a wide range of facies, from bioturbated limestones (> 75% CaCO_3) to laminated, C_{org} -rich (> 1 wt. %) black shales. The absence of any positive correlation provides little evidence at either site that diagenesis of P_{auth} into more soluble mineral phases occurred post-burial.

Two alternate hypotheses may be invoked to explain the trends observed in Figures 2.4 and 2.5. The first states that enhanced nutrient supply via terrestrial input may result in increased rates of primary production and therefore increased consumption of oxygen in the water column due to organic matter (OM) degradation. Increased recycling of P_{react} and subsequent decrease in the burial efficiency of P_{auth} mineral phases would result in relatively lower P_{react} and higher P_{det} values. If this hypothesis is valid, one would predict that increased P_{det} concentrations would be associated with increased $\text{C}_{\text{org}}/P_{\text{react}}$ values. Such a scenario would be consistent with past interpretations of oxygen-deficient conditions being associated with enhanced C_{org}

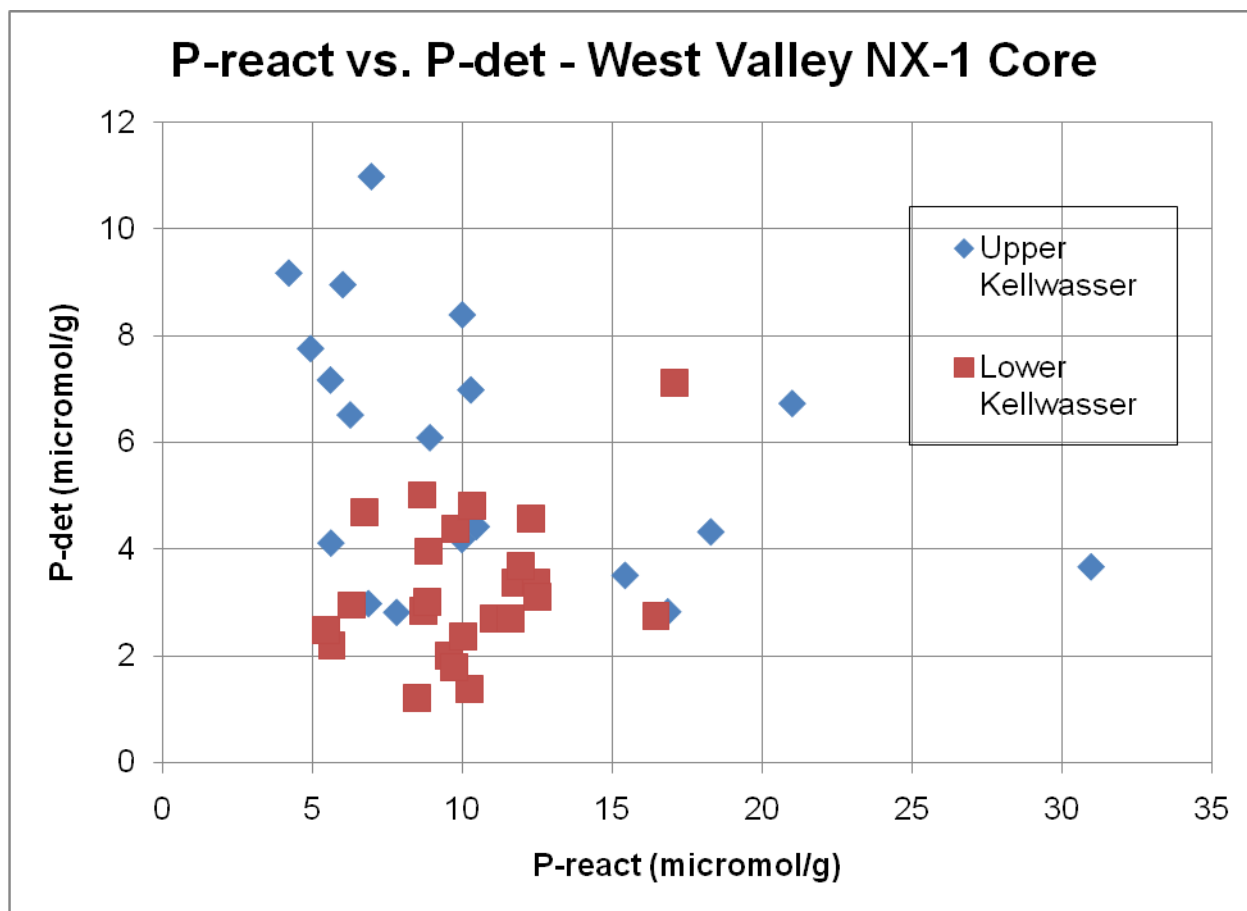


Figure 2.4. Cross plot of P_{react} vs. P_{det} from samples spanning the F – F biotic crisis from the West Valley Core. vs. P_{det} from samples spanning the F – F biotic crisis from the West Valley Core.

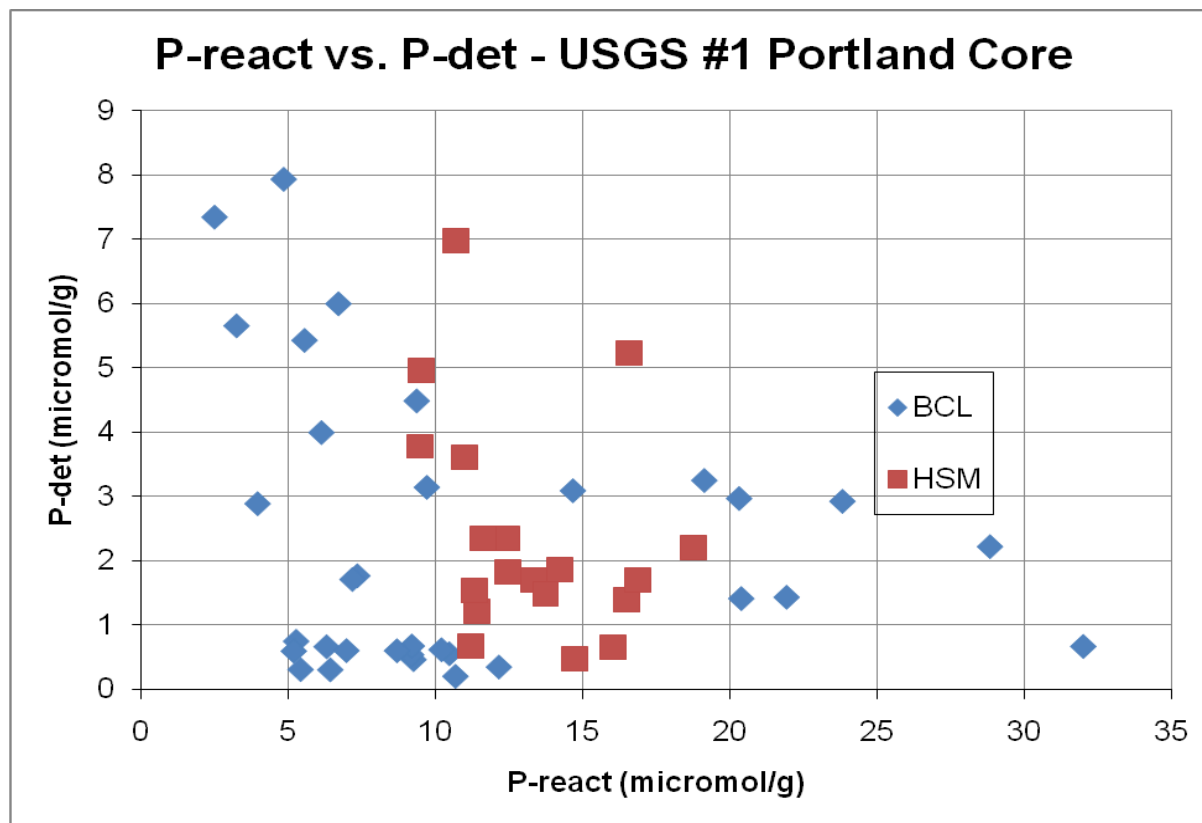


Figure 2.5. Cross plot of P_{react} vs. P_{det} from samples from the Portland Core. BCL samples are from the Bridge Creek Limestone Member of the Greenhorn Formation and represent deposition during and immediately following OAE 2. HSM samples are from the Hartland Shale Member of the Greenhorn Formation and represent deposition immediately prior to the onset of OAE 2.

burial efficiencies (Demailson and Moore, 1980) and enhanced recycling of P_{react} (Ingall et al., 1993), as well as with the suggestion that increased rates of primary production in the DAB were caused by an increased flux of terrestrially derived nutrients (Algeo et al., 1995; Algeo and Scheckler, 1998). However, a cross plot of $C_{\text{org}}/P_{\text{react}}$ vs. P_{det} from samples of both the West Valley and Portland Cores demonstrates no trends that support this hypothesis (Fig. 2.6).

An alternative hypothesis is that increased P_{det} accumulation is associated with an overall increase in terrestrial input that leads to relative dilution of P_{react} species that formed *in situ* in the marine sediments. The vague suggestion of decreasing maximum P_{det} concentrations associated with decreased P_{react} as observed in Figures 2.4 and 2.5 is consistent with this concept based on the assumption that increased P_{det} concentrations are associated with an overall increase in the flux of detrital material. If such a hypothesis is valid, changes in other detrital indicators should provide additional support.

Previous studies of laminated black shales spanning the F – F boundary have suggested that increased C_{org} burial in these shales was caused by enhanced nutrient delivery from the terrestrial realm resulting from increased chemical weathering rates due to the development of the first terrestrial forests (Algeo et al., 1995; Algeo and Scheckler, 1998). Analysis of a series of detrital proxies, such as Ti/Al and Na/K (Sageman et al., 2003), indicate that there may have been a relative increase in the flux of terrestrial material to the DAB prior to the F – F boundary event. Comparison of these proxies with P_{det} accumulation has demonstrated that P_{det} concentrations increase

(41% in Lower Kellwasser; 80% in Upper Kellwasser) along with increases in detrital proxies (see Chapter 5). This observation lends further support to the idea that trends in P_{det} in the West Valley Core correspond to changes in the flux of terrestrially derived nutrients and that P_{det} acts as a relative proxy for such processes. It also supports the hypothesis that the trend demonstrated in Figure 5 is related to dilution of P_{react} phases during intervals of enhanced accumulation of terrestrially derived material.

Proxy indicators for the OAE 2 interval in strata of the Portland Core (Sageman et al., 1997; Sageman et al., 1998) also indicate enhanced terrestrial accumulation in deposits with elevated concentrations of P_{det} (see Chapter 3). Such observations are most prevalent in HSM strata which have been interpreted to have been deposited during lower sea-levels than those of the BCL (Laurin et al., 2005; Laurin and Sageman, 2001). These observations, along with proxy evidence of high global temperatures and an enhanced hydrologic cycle (Forster et al., 2007; Huber et al., 2002; Schouten et al., 2003) as well as a major shift to more terrestrial $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values immediately preceding the onset of OAE 2 (Frijia and Parente, 2008) lend support to the hypothesis that the interval leading up to OAE 2 was characterized by high rates of chemical weathering resulting in larger terrestrial inputs. The trend of decreasing maximum P_{det} concentrations with increasing P_{react} observed in Figure 2.5 would therefore be expected with increased rates of terrestrial input to a shallow epicontinental seaway as dilution of reactive phases would occur with increased detrital accumulation.

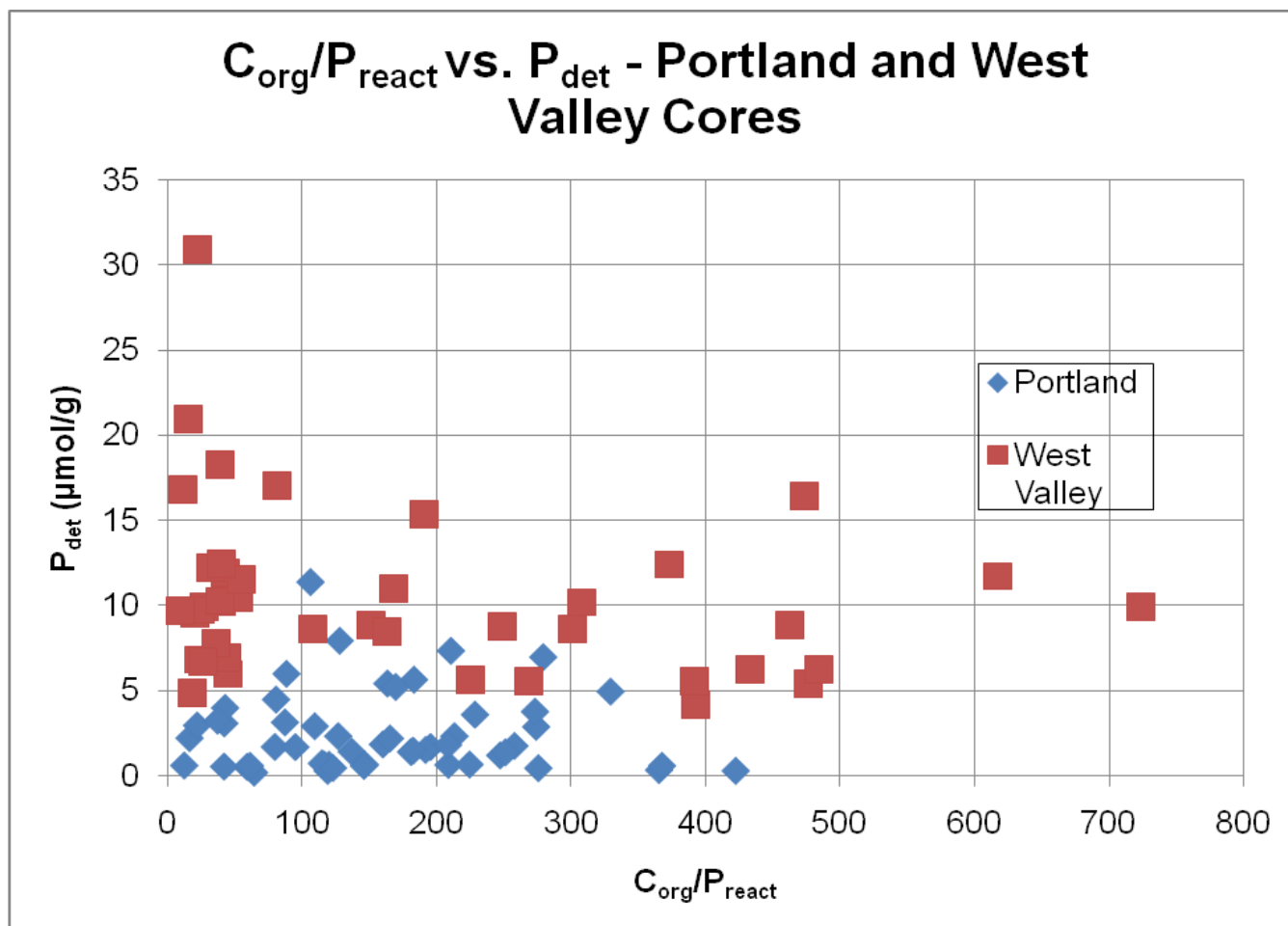


Figure 2.6. Cross plot of C_{org}/P_{react} vs. P_{det} from samples from the West Valley and Portland Cores.

2.3.2 Hemipelagic Marine Setting

C – T samples from ODP Site 1258 were deposited in a hemipelagic – pelagic marine setting in the tropical North Atlantic Ocean (Erbacher et al., 2004). Water depth estimates range between upper to middle bathyal. Deposits from this site in the OAE 2 interval are characterized by TOC concentrations over 20% (Erbacher et al., 2005). It has also recently been suggested that this may have been an area of active upwelling during the OAE 2 interval (Junium and Arthur, 2007). Thus, this site may represent a good opportunity for direct comparison to the Monterey Formation regarding the potential diagenesis of P_{auth} mineral phases.

Cross plots of P_{react} vs. P_{det} in deposits spanning OAE 2 from ODP Site 1258 demonstrate two distinct trends (Fig. 2.7). The first trend demonstrates little to no accumulation of P_{det} regardless of the concentration of P_{react} . The second trend demonstrates increasing P_{det} with increasing P_{react} very similar to the trend observed in the Monterey Formation (Figure 2.1). Deposits displaying this trend at Site 1258 have been interpreted to represent winnowed intervals resulting in high concentrations of phosphatic rich fish debris and nodules (Erbacher et al., 2004). I examine each of the trends described here separately in the next section.

Background Hemipelagic Marine Deposits

Deposits representing background hemipelagic sedimentation at the time of deposition from ODP Site 1258 display very low concentrations of P_{det} through varying concentrations of P_{react} (Fig. 2.7). This is the trend expected of deposits in middle to upper bathyal water depths as such environments occur far from terrestrial sources in

modern environments along passive continental margins. The same trend was also observed in the study of the Monterey Formation of Filippelli and Delaney (1995) in the siliceous facies: little evidence of P_{det} accumulation was observed despite varied concentrations of P_{react} . Lack of evidence for detrital accumulation in the Monterey Formation based on other geochemical proxies (Follmi et al., 2005) is consistent with the hypothesis that P_{det} , as defined by the SEDEX method, co-varies with other indicators of terrestrial input and is not misrepresented by diagenetic factors.

The total P concentrations in both the hemipelagic – pelagic siliceous facies of the Monterey Formation and in the C_{org} –rich black shale facies of ODP Site 1258 are very similar to those in modern hemipelagic facies across a wide range of depositional environments (Filippelli, 1997). Although only reported for one pelagic location in the compilation of Filippelli (1997), P_{react} concentrations in modern Equatorial Pacific sediments comprise above 98% of the total P deposited at this site. The average P_{react} concentrations of sediments in the hemipelagic facies at ODP Site 1258 is 94.3% with a range of values between 81.6 – 100 %. Thus, there is no evidence for significant post-burial diagenesis of P_{auth} to more soluble mineral phases in hemipelagic facies spanning the C – T interval at this locale.

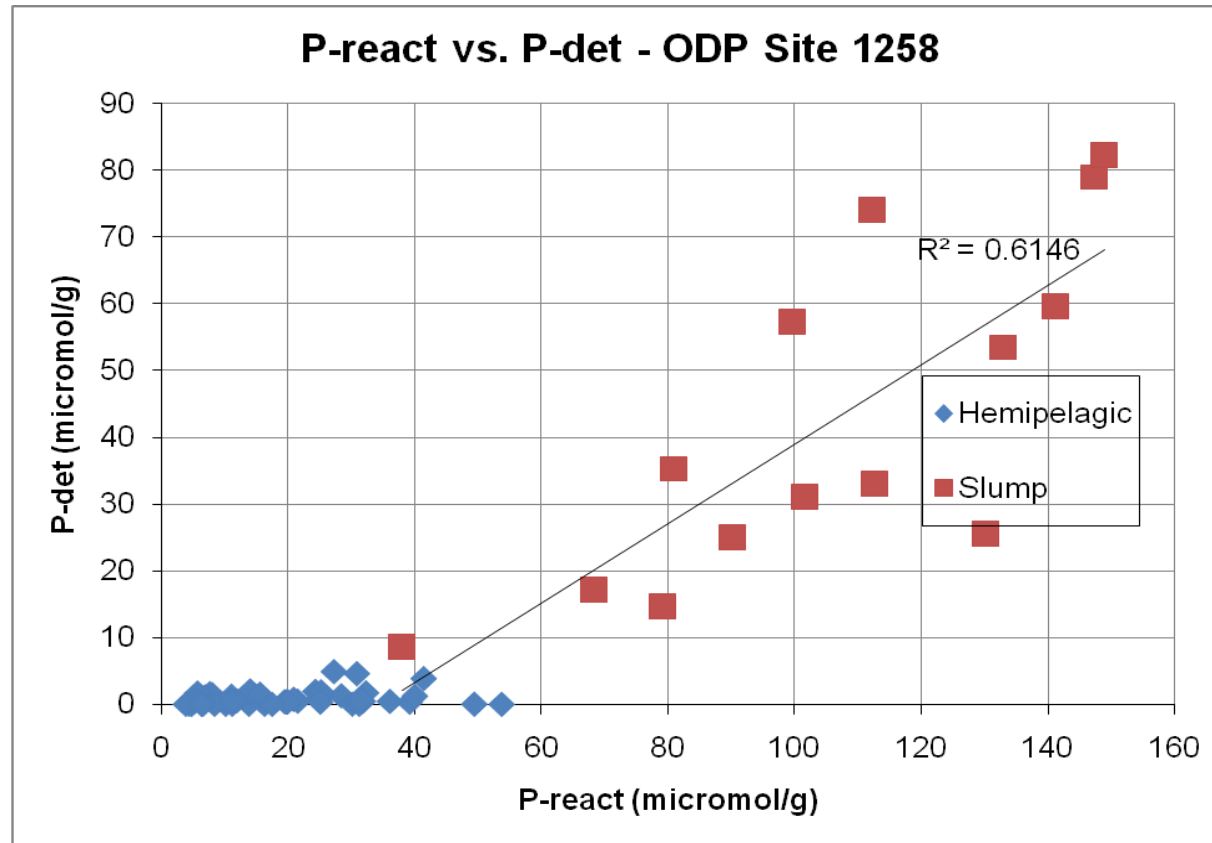


Figure 2.7. Cross plot of P_{react} vs. P_{det} from samples spanning OAE 2 at ODP Site 1258. Samples representing hemipelagic marine deposits are characterized by C_{org} -rich, laminated black shales (Erbacher et al., 2005; Erbacher et al., 2004). Samples representing winnowed facies show enrichments in shell material, fish debris, and phosphatic nodules (Erbacher et al., 2004).

Winnowed Facies

C – T strata from ODP Site 1258 contain a number of 1 – 5 cm thick beds characterized by high concentrations of shell material, phosphatic fish scales and bones, and phosphatic nodules (Erbacher et al., 2004). These facies are interpreted to have been deposited as a result of winnowing of fine grained sediments associated with background sedimentation (Erbacher et al., 2004). P concentrations in these deposits show a linear relationship between increasing P_{react} and increasing P_{det} (Fig. 2.7). This trend is very similar to that observed by Filippelli and Delaney (1995) in the phosphatic shales of the Monterey Formation (Fig. 2.1). It has since been suggested that the phosphatic deposits in the Monterey Formation may also have been a result of winnowing associated with gravity flow processes (Follmi et al., 2005).

The lithology of the so-called winnowed deposits from ODP Site 1258 may provide the explanation for the linear relationship between increasing concentrations of P_{react} and P_{det} . Many of the major components of these deposits either provide a surface for P to accumulate or contain large concentrations of P in their mineral structure. It has been demonstrated that shell material provides an excellent surface for iron oxide coatings and hence nucleation sites for accumulation of P_{ox} in shallow marine sediments (Sherwood et al., 1987). A high concentration of such shell material in deposits formed under oxygenated conditions may thus provide a mechanism for increased burial of P_{react} in a hemipelagic marine setting.

Fish debris is also a major component of the so-called winnowed deposits at ODP Site 1258. It is widely recognized that such material contains a significant

concentration of biogenic apatite. The SEDEX method includes dissolution of such material and records it as P_{auth} . In some modern environments it has been recognized that accumulations of such fish debris can be significant enough to require an additional step in the SEDEX method in order to separate such material (Babu and Nath, 2005; Schenau and De Lange, 2000; Schenau and De Lange, 2001; Schenau et al., 2005; Slomp et al., 2004). In studies of the Monterey Formation (Filippelli and Delaney, 1995; Follmi et al., 2005) this method had not been applied. I applied this additional step to two winnowed samples and two samples representative of background hemipelagic deposition (Fig. 2.8). From these measurements it is demonstrated that there is an order of magnitude increase in the average fish debris concentrations between winnowed and background hemipelagic deposits (average P_{fish} winnowed deposits = $21.8 \mu\text{mol/g}$; average P_{fish} hemipelagic deposits = $2.08 \mu\text{mol/g}$).

Phosphatic nodules are also composed of P_{auth} mineral phases and occur in high concentrations in both the winnowed deposits of ODP Site 1258 (Erbacher et al., 2004) and the phosphatic shales of the Monterey Formation (Filippelli and Delaney, 1995; Follmi et al., 2005). Thus, many of the lithologic components comprising the sediments demonstrating a linear trend between increasing P_{auth} and P_{det} (Figs. 2.1 and 2.7) are highly concentrated in P-bearing phases that would be measured as P_{auth} when

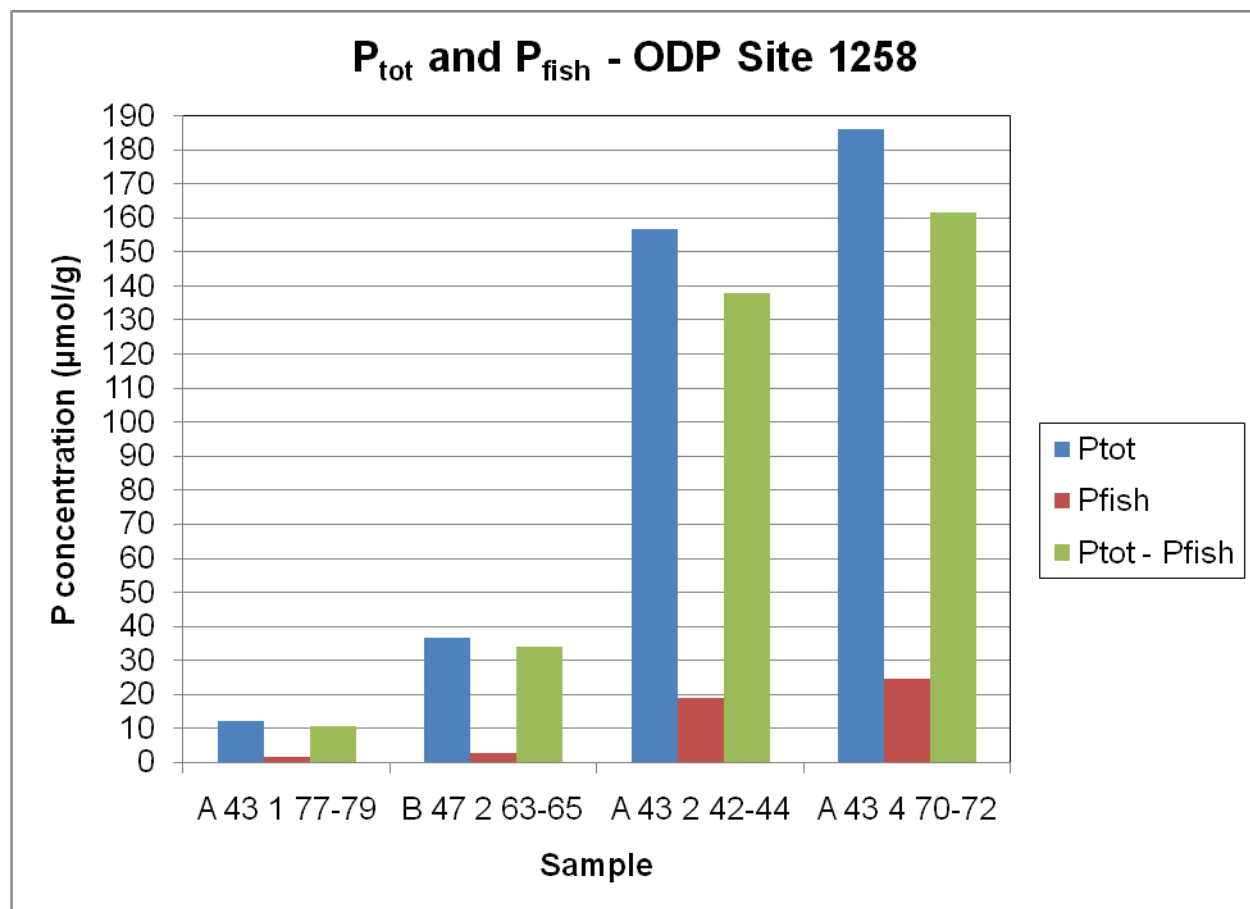


Figure 2.8. Bar graph demonstrating the increased concentrations of P_{tot} and P_{fish} in the winnowed deposits versus the background hemipelagic deposits at ODP Site 1258.

Samples A 43 1 77-79 and B 47 2 63-65 are representative background hemipelagic deposits while samples A 43 2 42-44 and A 43 4 70-72 are representative winnowed deposits.

utilizing the SEDEX method. In general, these unique deposits are characterized by extraordinarily high concentrations of P_{react} at both locales.

In a comprehensive study comparing P accumulation across a wide range of modern depositional environments, it was demonstrated that in non-phosphogenic settings, average total P concentrations rarely exceed 30 $\mu\text{mol/g}$ (Filippelli, 1997). This includes sites from the pelagic open ocean and non-upwelling continental margins. In their study of the phosphatic shales of the Monterey Formation, Filippelli and Delaney (1995) demonstrated deposits with total P concentrations ranging between 0.5 – 4 wt. % (161 – 1290 $\mu\text{mol/g}$). Such concentrations are much more similar to those found in the modern phosphogenic deposits off of Baja, California (Sundby et al., 1992) than to any values associated with hemipelagic marine sedimentation. Total P concentrations of the winnowed deposits at ODP Site 1258 are also higher than those of normal hemipelagic sediments in marine environments with values ranging between 50 – 240 $\mu\text{mol/g}$.

Collectively, the observations summarized above suggest an explanation for the strong positive correlation between P_{auth} and P_{det} that characterizes the Miocene and Cretaceous winnowed facies. In each case it appears that sediment condensation processes have resulted in anomalously high concentrations of biogenic P-bearing material such as fish scales, bones, and teeth. In fact, these high concentrations suggest that the winnowed facies of ODP Site 1258 are actually in-place winnowed horizons, perhaps the result of some kind of contour current. Removal of fine-grained sediment and concentration of phosphatic material in these horizons results in total P levels are so high that they likely saturate the SEDEX extraction process designed to

measure P_{auth} mineral phases, resulting in misrepresentation of biogenic P and phosphatic nodule material as P_{det} .

Results from ODP Site 1258 suggest a possible threshold of P_{react} concentrations that may result in an oversaturation of the SEDEX step designed to dissolve P_{auth} minerals. Below total P concentrations of 50 $\mu\text{mol/g}$, there are minimal concentrations of P_{det} . However, once total P concentrations reach values above 50 $\mu\text{mol/g}$ a linear trend is seen between P_{react} and P_{det} . Samples of the siliceous facies in the Monterey Formation also show total P concentrations of less than 50 $\mu\text{mol/g}$ whereas those of the phosphatic shales have some of the highest P_{auth} concentrations ever reported (Filippelli and Delaney, 1995). Therefore, it is proposed that oversaturation of the SEDEX step designed to dissolve P_{auth} mineral phases may occur when concentrations of such phases exceed 50 $\mu\text{mol/g}$. Further testing is needed to confirm this threshold value.

2.3.3 Comparison to Ti/Al

Demonstrating that P_{det} mineral phases are in fact derived from terrestrial sources is an important first step towards developing the argument that it can serve as a proxy for terrestrially derived P to the marine realm. However, if it could be demonstrated that such mineral phases have a positive correlation with other known detrital proxies, such a hypothesis becomes stronger. Here, I present a cross plot of P_{det} versus Ti/Al from samples of the USGS #1 Portland Core and NX-1 West Valley core (Fig. 2.9). Ti/Al is chosen as the detrital proxy to plot P_{det} versus as increases in this ratio have been utilized to reflect enhanced delivery of terrestrial material from riverine sources (Bertrand et al., 1996; Murray et al., 2000; Murray and Leinen, 1996).

Hence, a positive correlation between Ti/Al and P_{det} will not only support the hypothesis that P_{det} is derived from terrestrial sources, but also that it is being sourced via riverine processes which also would be transporting dissolved, bioavailable P. Such a positive correlation is demonstrated from the samples of this study in Figure 2.9 ($R^2 = 0.15$). Therefore, at least in the case of the KWIS and DAB, it can be reasonably assumed that increased P_{det} accumulation can be a proxy for enhanced delivery of bioavailable P to marine surface waters.

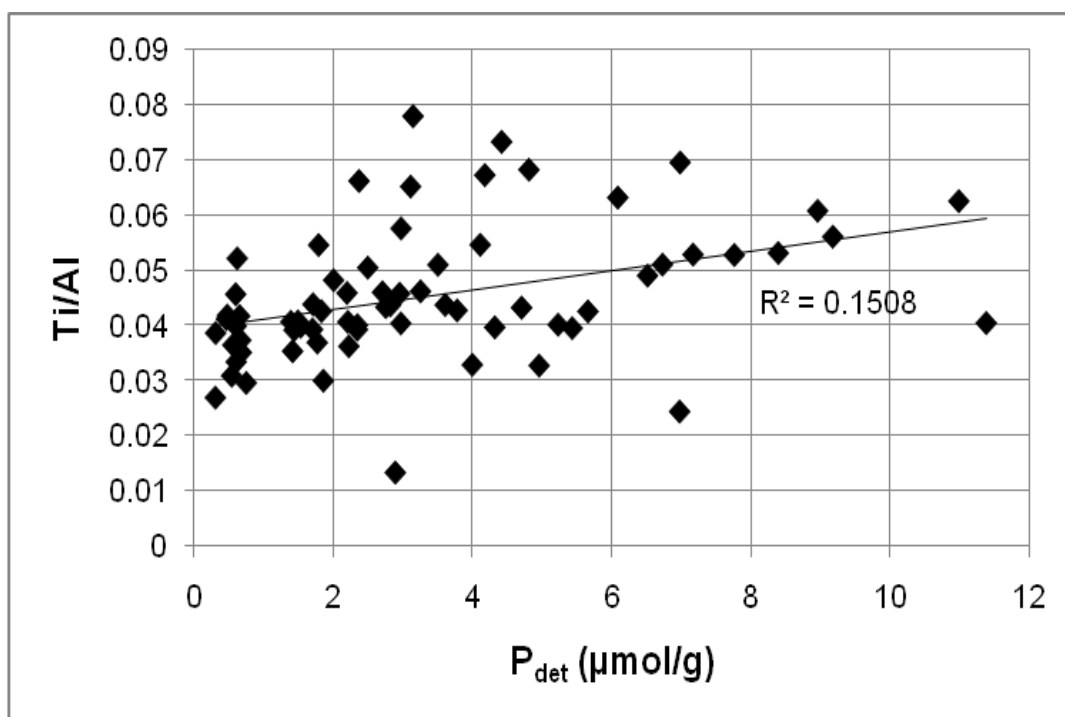


Figure 2.9. Cross plot of P_{det} vs. Ti/Al for samples from the USGS #1 Portland Core and NX-1 West Valley Core. Trace element concentrations for the Portland Core are obtained from Sageman et al. (1987, 1988) while those from the West Valley Core are obtained from Sageman et al. (2003).

2.4 IMPLICATIONS

If P_{det} values determined for ancient marine deposits, as measured with the SEDEX method, were consistently compromised by post-burial addition of diagenetically altered P_{auth} , reconstruction of ancient P reservoirs using this method would be biased. One of the most important aspects of the SEDEX method is its ability to differentiate the P_{react} phases from non-reactive P_{det} . If such information could not be discerned, then prior methods (Aspila et al., 1976) would provide the same information regarding total P in a much less time intensive procedure. The data presented in this study, however, suggest an alternative explanation to the decarboxylation hypothesis (Shemesh, 1990). The results appear consistent for a variety of depositional environments and geologic ages. These observations support results from prior research that indicate there is no correlation between the crystallinity indices of biogenic apatite minerals and other diagenetic indicators, including $\delta^{18}\text{O}$ of the apatites and rare earth element concentrations, from samples across a broad range of depositional environments and time periods (Puceat et al., 2004). Collectively, these data suggest that depositional processes leading to anomalous concentration of biogenic P may result in total P_{auth} levels that oversaturate the SEDEX method and provide no support for the post-burial conversion of P_{auth} to less soluble phases that chemically resemble P_{det} .

This negative evidence for the decarboxylation hypothesis has significant implications for interpretation of P cycling in the geologic past. Much debate has centered on the source of the nutrients necessary to cause increased rates of marine

primary productivity interpreted for events like the C- T OAE 2 and F – F black shales, as well as other intervals of enhanced C_{org} burial. Much of the research regarding nutrient supplies for these events (e.g., Algeo et al., 1995; Algeo and Scheckler, 1998; Handoh and Lenton, 2003; Mort et al., 2007; Murphy et al., 2000a; Murphy et al., 2000b; Nederbragt et al., 2004; Sageman et al., 2003) has focused on the role of P based on the belief that over geologic timescales, P acts as the key biolimiting nutrient in the marine realm (Bjerrum and Canfield, 2002; Tyrrell, 1999).

Of particular importance has been debate regarding the role of the terrestrial supply of nutrients vs. recycling of P under oxygen-deficient conditions during intervals of increased primary production. A recent study of the marine P cycle during OAE 2 suggested that increased productivity was a result of increased recycling of P under oxygen-deficient conditions in the water column (Mort et al., 2007). In their study, Mort et al. (2007) utilize the decarboxylation hypothesis to argue that P_{det} is, in fact, diagenetically altered P_{auth} and therefore discount the use of P_{det} as a potential proxy for terrestrially derived nutrient flux. However, this interpretation fails to explain increased primary productivity prior to the onset of the event, which is characterized by increased burial rates of all P phases, but low C_{org} burial, thus indicating increased primary production in an oxic ocean. These observations suggest that a terrestrial source of nutrients may have initiated the C – T event.

Based on the observations of this study, increased rates of P_{det} accumulation in ancient marine deposits provide a legitimate proxy for enhanced terrestrial nutrient supply possibly resulting in increased rates of primary production in the global ocean

during intervals of the geologic past. Such a conclusion may have a broad impact on our current understanding of the coupled C and P cycles. It has been widely recognized that variations in the burial efficiency of P_{react} phases may result in changes in the rates of marine primary production and hence burial of C_{org} . However, if P_{det} accumulation does in fact represent an accurate proxy for the flux of terrestrially derived dissolved P, then there is also a link between P_{det} and chemical weathering, and hence another sink for atmospheric CO_2 . Therefore, the ability to accurately differentiate between the different sedimentary P phases in ancient marine deposits should continue to contribute important knowledge to our understanding of the global C cycle, as well as the marine P cycle during intervals of the geologic past.

2.5 CONCLUSIONS

This study applied the SEDEX method to samples spanning the Cenomanian - Turonian OAE 2 and Frasnian - Famennian black shales in order to test the decarboxylation hypothesis. The results support previously published data from Raman spectroscopy of samples spanning the entire Phanerozoic, and provide no supporting evidence for the decarboxylation hypothesis. Based on these observations, it is concluded that utilization of the SEDEX method provides important information regarding P cycling in the marine realm throughout the geologic past that cannot, at this time, be replicated by other methodologies. In particular, positive correlations between P_{det} accumulation and other terrestrial and weathering proxies do, in fact, provide a potential proxy for terrestrially derived bioavailable P during intervals of increased rates of marine primary production.

CHAPTER 3

PHOSPHORUS SOURCES TO MARINE SURFACE WATERS AND THEIR ROLE ON ORGANIC CARBON BURIAL DURING OCEANIC ANOXIC EVENT 2

3.1 INTRODUCTION

The mid- to late Cretaceous was characterized by numerous periods of widespread deposition of organic carbon (C_{org}), interpreted to represent expansion of oxygen-deficient conditions in the global ocean (e.g., Arthur et al., 1985; Schlanger et al., 1987; Schlanger and Jenkyns, 1976 and others). Such intervals have been termed Oceanic Anoxic Events (OAE). Studies of Cretaceous OAEs have greatly added to our understanding of the global carbon cycle in the geologic past (Arthur et al., 1985; Jenkyns, 1980; Kump and Arthur, 1999; Schlanger and Jenkyns, 1976). One of the most widespread and extensively studied of these OAEs is the Cenomanian – Turonian (C – T) OAE 2.

The C – T interval is characterized by the ubiquitous occurrence of finely laminated facies with multiple geochemical indicators of anoxic to euxinic bottom water conditions (Arthur et al., 1988; Arthur et al., 1987; Jenkyns, 1980; Kolonic et al., 2005; Kuypers et al., 2004; Kuypers et al., 2002; Meyers, 2006; Meyers et al., 2003; Meyers et al., 2005; Orth et al., 1993; Schlanger et al., 1987; Schlanger and Jenkyns, 1976; Scopelliti et al., 2004). Within the C – T interval is a 2 – 6 ‰ positive $\delta^{13}C$ excursion in both carbonates and organic matter (Bowman and Bralower, 2005; Gustafsson et al., 2003; Kump and Arthur, 1999; Pratt, 1985; Sageman et al., 2006; Scholle and Arthur, 1980; Tsikos et al., 2004; Voigt et al., 2006; Wan et al., 2003) defines the relatively

short-lived OAE 2, which has been interpreted to represent a massive global increase in the burial and preservation of ^{12}C enriched organic matter (OM). For many years the question of whether enhanced OM burial was a consequence of elevated primary production (Pedersen and Calvert, 1990) or enhanced oxygen deficiency due to water column stratification (Demaison and Moore, 1980) has attended the study of Cretaceous OAEs.

Within the last decade most researchers have settled on production as the primary mechanism driving OAE 2 (e.g., Kuypers et al., 2002 and others). It is therefore important to understand from where the nutrients necessary to initiate and maintain such production were sourced. Several hypotheses have been put forth and continue to be debated in the literature. Such hypotheses include changes in the rates of upwelling in the global ocean due to sea-level rise (Arthur et al., 1987) or opening of the gateway between the North and South Atlantic Oceans (Summerhayes, 1987), increased delivery of micro-nutrients, such as iron, due to increased hydrothermal activity (Sinton and Duncan, 1997; Snow et al., 2005), nutrient release from shallow marine sediments during sea-level rise (Bjerrum et al., 2006), greater rates of chemical weathering resulting in an elevated terrestrial flux (Erbacher et al., 1996; Frijia and Parente, 2008; Weissert, 1989), and enhanced regeneration during OM degradation under oxygen-deficient waters (Mort et al., 2007; Nederbragt et al., 2004).

In this study I use the SEDEX sequential extraction procedure (Anderson and Delaney, 2000; Ruttenberg, 1992) to assess how variations in the delivery of phosphorus (P) to marine surface waters may have effected C_{org} accumulation prior to and during

OAE 2. Phosphorus is chosen as the nutrient to examine based on the belief that it is the ultimate biolimiting nutrient over geologic timescales (Bjerrum and Canfield, 2002; Tyrrell, 1999). Results obtained from SEDEX allow direct interpretations regarding the hypotheses of an increased flux of terrestrially derived nutrients (see Chapter 2) and enhanced nutrient cycling (Filippelli et al., 2003; Mort et al., 2007; Rittenberg and Goni, 1997; Schenau and De Lange, 2001; Slomp et al., 2002; Slomp et al., 2004) during the C – T interval. While direct examination of other potential mechanisms for P delivery to marine surface waters is outside the scope of this study, their potential influence on the marine P budget during the OAE 2 interval will be qualitatively considered.

Samples from three sites were analyzed: two localities (USGS #1 Portland Core and Ram Falls outcrop section) occur within the Cretaceous Western Interior Basin (KWIS; Fig. 3.1) and a third locality is Site 1258 from ODP Leg 207, within the tropical North Atlantic Ocean (Fig. 3.1). Together these sites span nearly 43° of latitude (Table 3.1) and sample deep oceanic as well as shallow epeiric environments. This distribution of localities allows for the evaluation of variations in terrestrial nutrient supply in shallow marine settings spanning northern tropical to temperate climate belts, as well as the role of enhanced P regeneration in a productivity – anoxia feedback (PAF) type mechanism (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Ingall et al., 1993; VanCappellen and Ingall, 1994) in open ocean settings prior to and during deposition of OAE 2.

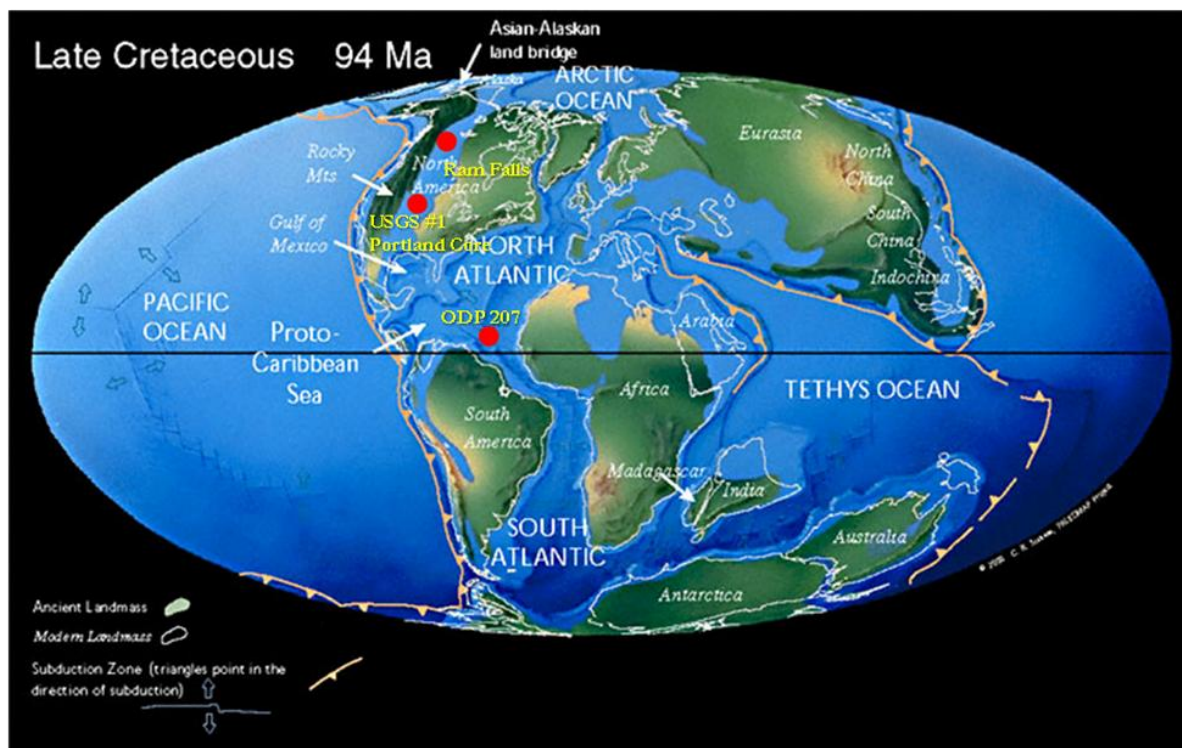


Figure 3.1. Paleogeographic map of the Late Cretaceous showing the locations of the USGS #1 Portland Core, Ram Falls outcrop section, and ODP Leg 207 of which Site 1258 was a part of. Map acquired from www.scotese.com.

3.2 Geologic Background

All three sites examined in this study span the intervals preceding, including, and following OAE 2. Samples from the USGS #1 Portland Core represent deposition in a shallow marine epicontinental seaway at sub-tropical paleolatitudes, therefore possibly accumulating in a climate zone with high evaporation of marine surface waters. Intervals studied from this site include the Hartland Shale (HSM) and Bridge Creek Limestone (BCL) members of the Greenhorn Formation. The HSM is a 12 m thick, C_{org} -rich calcareous shale. Concentrations of C_{org} range between 1 – 5 wt. % while relatively elevated redox proxies such as Mo (e.g., Meyers et al., 2005) and detrital proxies such as Ti/Al, Na/K, and K/(Fe + Mg) suggest deposition in a shallow, restricted seaway sensitive to fluctuations in terrigenous, pelagic sediment supply, and OM production. The BCL is a 12 m thick section that includes the entire OAE 2 interval and the period immediately following this event. It consists of decimeter-scale couplets of laminated to slightly burrowed C_{org} -rich marlstones and highly burrowed C_{org} -poor limestones (Elder et al., 1994; Sageman et al., 1997; Sageman et al., 1998).

Both the Ram Falls outcrop section and ODP Site 1258 also span the intervals preceding, including, and following OAE 2. The Ram Falls section was deposited in the same shallow epicontinental seaway as the USGS #1 Portland Core but at a more temperate paleolatitude thus suggesting a climate characterized by higher rates of precipitation than the Portland core site. Lithologies of the Ram Falls section primarily

Table 3.1 Locality Data of Sites Studied

Site	Latitude (°N)	Longitude (°W)
USGS #1 Portland Core	38°22.6'	105°1.3'
Ram Falls	52°5.35'	115°50.18'
ODP Site 1258	9°26'	54°44.98'

include moderately C_{org} –rich (1 – 3 wt. %) mudstone to silty mudstone facies indicative of shallow marine deposition. ODP Site 1258, however, was deposited in middle to upper bathyal water depths at tropical paleolatitudes in the North Atlantic Ocean (Erbacher et al., 2004). Thus deposits from this section represent hemipelagic to pelagic deposition in a tropical environment potentially influenced by equatorial upwelling. Facies collected at this site are primarily composed of several meter thick, laminated, C_{org} –rich (up to 20 wt. %) black shales with occasional decimeter scale C_{org} - poor limestones (Erbacher et al., 2005; Erbacher et al., 2004). Detailed locality data is provided for each site in Table 3.1.

3.3 METHODS

Phosphorus analyses on all samples in this study were completed utilizing the SEDEX sequential extraction procedure (Anderson and Delaney, 2000; Ruttenger, 1992). A summary of this method and the phases that are extracted by it is presented in Chapter 1 of this dissertation and in Figure 1.1. Calculations of C_{org}/P_{react} are achieved by dividing the concentrations of each in weight percent and dividing that ratio by the atomic mass ratio of C and P (12/31). P_{det} is considered a non-reactive phase and has been demonstrated to represent a potential proxy for the delivery of terrestrially derived P to shallow marine environments (see Chapter 2). Evaluations of P_{react} accumulation and C_{org}/P_{react} ratios, along with redox sensitive elemental data where available (USGS #1 Portland Core), allow for the determination of redox controlled P cycling within the marine realm and evaluation of the potential of a PAF type model in supplying bioavailable P to the photic zone during OAE 2.

Parameters such as $\delta^{13}C_{org}$, C_{org} , $CaCO_3$, and other elemental data have been published previously for the entire study interval based on analysis of samples from the USGS #1 Portland Core (Sageman and Lyons, 2003; Sageman et al., 2006; Sageman et al., 1997; Sageman et al., 1998). Carbon isotope data for the Ram Falls outcrop section was obtained from D. Grocke (personal communication). Concentrations of C_{org} and $CaCO_3$ for Ram Falls samples data were collected utilizing standard coulometric techniques (Huffman, 1977). Organic C concentration and $\delta^{13}C_{org}$ data for ODP Site 1258 was obtained from previously published results (Erbacher et al., 2004). Carbonate concentration data was measured via standard coulometric techniques (Huffman,

1977). No elemental data is currently available for the Ram Falls or ODP Site 1258 locales.

Concentration data within this study are converted to accumulation rates via utilization of a C – T timescale including radioisotope and astronomical chronologies (Gradstein et al., 2004; Sageman et al., 2006). Dry bulk densities for samples from the USGS #1 Portland Core and Ram Falls were measured on samples of representative lithologies from the site (USGS #1 Portland Core) or the Ribstone Core site, which is in close proximity to the Ram Falls outcrop section. Average density values for limestones (>75 wt. % CaCO_3) at the Portland Core site were 2.55 g/cm^3 , marlstones (50 – 74 wt. % CaCO_3) were 2.5 g/cm^3 , and mudstones (<50 wt. % CaCO_3) were 2.4 g/cm^3 . Average densities for the carbonate – poor mudstones of the Ram Falls section were 2 g/cm^3 . Density values for ODP Site 1258 were obtained from published gamma ray attenuation (GRA) measurements (Erbacher et al., 2004). For BCL deposits sedimentation rates were previously estimated using astronomical chronologies (Meyers et al., 2001; Sageman et al., 2006), whereas HSM sedimentation rates are calculated utilizing the geologic timescale of Gradstein et al. (2004). At the Ram Falls site and ODP site 1258 sedimentation rates are estimated by dividing the thickness of the OAE 2 interval as defined by the carbon isotope excursion by the 600 kyr interval of OAE 2 (Sageman et al., 2006). Based on the lack of observations of any discernable hiatus, it is assumed that sedimentation rates remained constant throughout the study interval at both of these sites.

3.3 RESULTS

3.3.1 USGS #1 Portland Core

Concentration data of the P phases defined by the SEDEX method, as well as C_{org} concentrations and C_{org}/P_{react} values, are given in Appendix I and plotted in Figure 3.2. Concentrations of C_{org} range between 0.14 – 5.32 wt. % with the lowest values occurring in burrowed limestones deposited during OAE 2 and highest values in the calcareous shales of the HSM and post-OAE 2 BCL. A similar trend is observed for P_{react} . Values range between 2.5 – 32 $\mu\text{mol/g}$ with lowest values in deposits of OAE 2 and highest in the HSM and post-OAE 2 BCL. Concentrations of P_{det} range between 0.2 – 11.4 $\mu\text{mol/g}$, with the highest values in the uppermost HSM and lower BCL and lowest values in deposits of the post-OAE 2 BCL. Average values of each phase for the HSM and BCL are presented in Table 3.2 for comparison to other sites from this study and modern depositional environments.

The MAR data demonstrates a decrease in accumulation rates of both the P_{react} (ave. HSM = 70 $\mu\text{mol/cm}^2/\text{kyr}$; ave. BCL = 21 $\mu\text{mol/cm}^2/\text{kyr}$) and P_{det} (HSM = 15 $\mu\text{mol/cm}^2/\text{kyr}$; BCL = 5 $\mu\text{mol/cm}^2/\text{kyr}$) phases from the HSM to the BCL (Fig. 3.3). This trend is primarily a reflection of changes in sedimentation rate through the section (Fig. 3.3) as average concentrations do not vary significantly between the two stratigraphic units (Table 3.2). However, there is a significant decline in both concentration and accumulation rates of P_{react} during OAE 2 relative to the HSM and post-OAE 2 BCL

Figure 3.2. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$ (Pratt, 1993; Sageman et al., 2006), C_{org} concentration (Sageman and Lyons, 2003; Sageman et al., 1997; Sageman et al., 1998), P species concentrations, and $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ values for the USGS #1 Portland Core deposits in the HSM and BCL. Shaded interval represents deposits of OAE2.

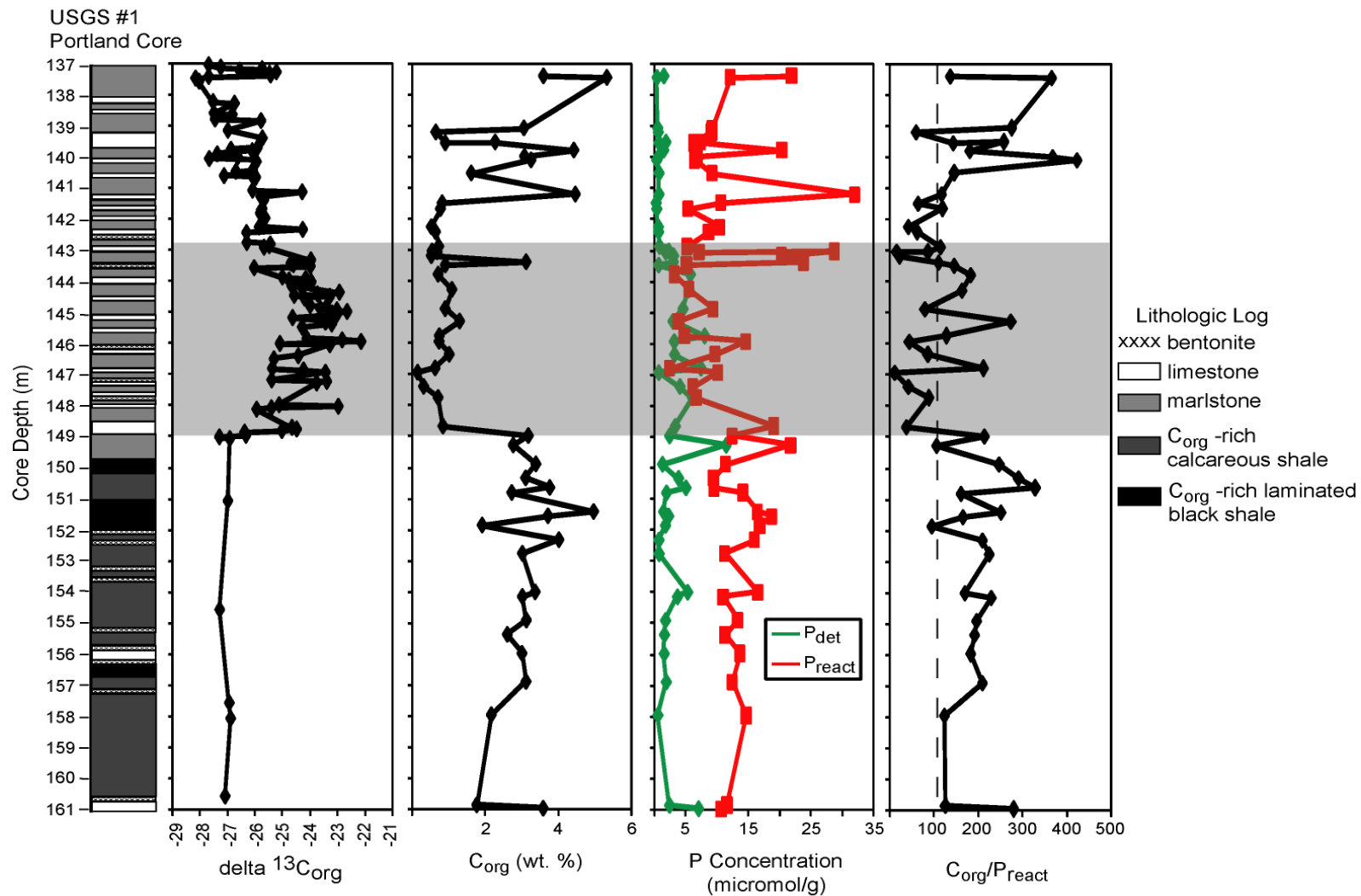


Figure 3.2.

Figure 3.3. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$ (Pratt, 1993; Sageman et al., 2006), C_{org} concentration (Sageman and Lyons, 2003; Sageman et al., 1997; Sageman et al., 1998), P species concentrations, and $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ values for the USGS #1 Portland Core deposits in the HSM and BCL. Shaded interval represents deposits of OAE2.

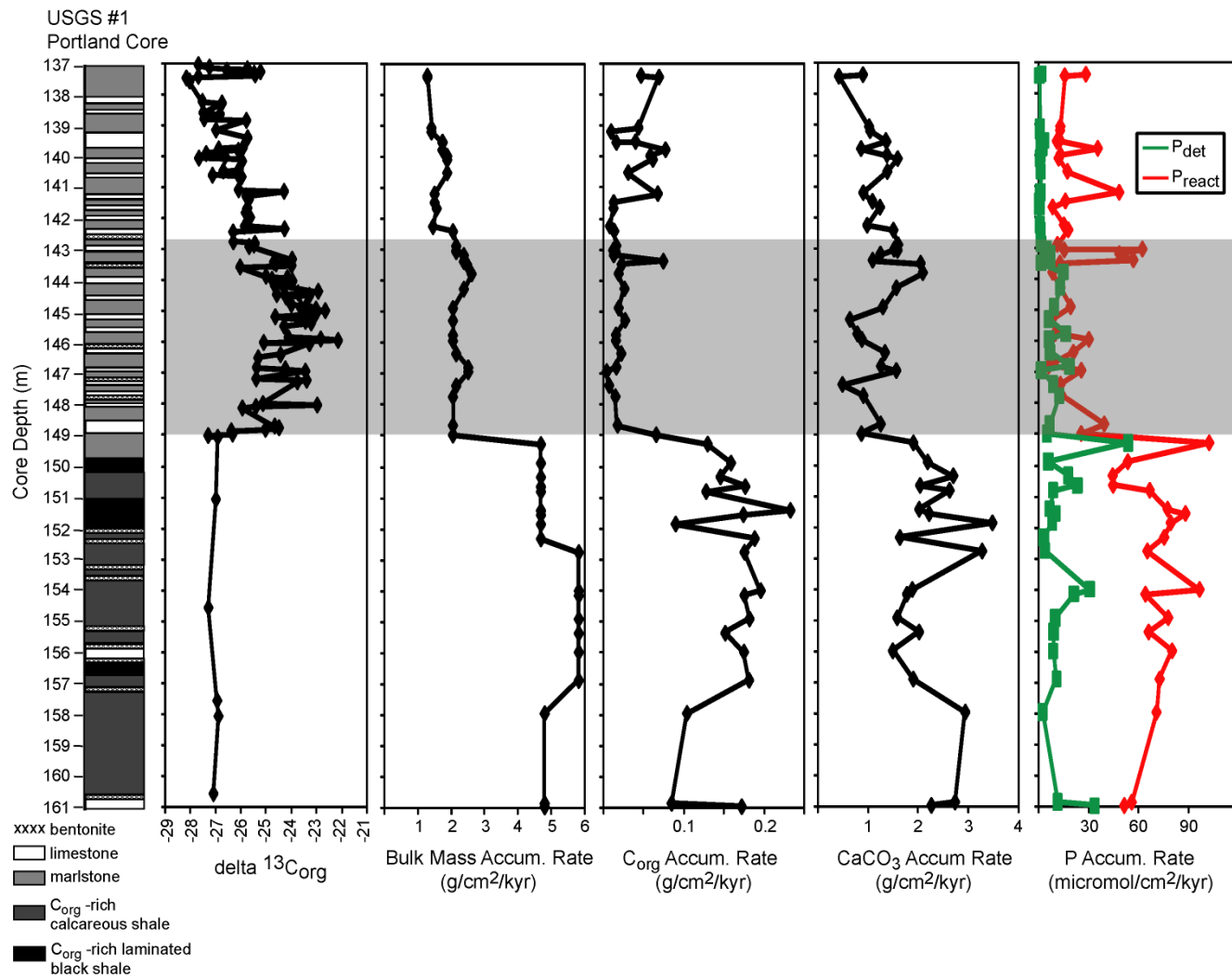


Figure 3.3.

**TABLE 3.2 COMPARISON OF MODERN P_{auth} ACCUMULATION RATES TO
ANCIENT DEPOSITS FROM THIS STUDY**

Location	Site	P_{auth} accumulation ($\mu\text{mol}/\text{cm}^2/\text{kyr}$)	Reference
Modern Settings			
Peru Margin	upwelling	1220	a
Baja, California Slope	upwelling	1110	b
Iberian margin (shelf and slope)	upwelling (seasonal)	33 - 189	c
Iberian margin (base)	upwelling (seasonal)	2170	c
Long Island Sound	non-upwelling	139	d
California margin	non-upwelling	44	e
Goban Spur	non-upwelling	11	f
Japan Sea upper margin	non-upwelling	86	g
Japan Sea lower margin	non-upwelling	30 - 110	g
Japan Sea Ulleung basin	non-upwelling	13 - 82	g
This Study			
USGS #1 Portland Core	shallow epicontinental	7 - 138	
Ram Falls	shallow epicontinental middle to upper	21 - 39	
ODP Site 1258	bathyal	4 - 125	

a. (Froelich et al., 1988); b. (Schuffert et al., 1998); c. (van der Zee et al., 2002); d. (Ruttenberg and Berner, 1993); e. (Kim et al., 1999); f. (Slomp et al., 1996a); g. (Cha et al., 2005).

intervals (~ 74% decline in accumulation relative to HSM; ~25% decline in accumulation relative to post-OAE 2 BCL). Possible mechanisms for the decline in P_{react} during OAE 2 at this locale are discussed further in Chapter 4.

Calculated P_{react} accumulation rates in the HSM are comparable to modern non-upwelling outer continental shelf environments (Cha et al., 2005; Kim et al., 1999) while those of the BCL are more similar to modern basinal to extreme outer shelf pelagic marine environments (Cha et al., 2005; Slomp et al., 1996a) (Table 3.2). Variations in P_{react} accumulation rates between the HSM and BCL facies are thus consistent with the deepening of the seaway across the boundary between these two units and lend further support to previous interpretations of a significant sea-level rise through the study interval (Arthur and Sageman, 2005; Laurin et al., 2005; Laurin and Sageman, 2001). However, the change in P_{react} burial rates can not be attributed solely to a Waltherian shift in facies. Although P_{react} burial is similar to rates in modern basinal environments, productivity rates during deposition of the BCL have been estimated to reflect those of modern continental shelves (Meyers et al., 2005).

Detrital P accumulation rates are also greatest in the HSM, become slightly reduced during OAE 2, and then approach values at or near zero in the BCL interval immediately following the event (Fig. 3.3). Although to my knowledge there are no modern environments in which P_{det} accumulation rates have been calculated, the change in rates from the HSM to the BCL is also consistent with significant sea-level rise through the study interval, assuming P_{det} represents a terrestrially derived mineral phase (see Chapter 2).

Values of C_{org}/P_{react} are enriched relative to Redfield throughout most of the pre- and post- OAE 2 intervals (Fig. 3.2) with average values of 198 and 202, respectively. Within the OAE 2 interval, however, ratio values are generally at or less than Redfield (ave. = 102), especially in the early stages of the event.

Phosphorus concentrations and C_{org}/P_{react} values were compared with P_{tot}/Ti and Mo concentrations throughout both the HSM and BCL (Fig. 3.4). Values of P_{tot}/Ti have been utilized in modern marine sediments as a productivity proxy because it normalizes P burial relative to terrestrial input, thus eliminating P sourced to marine sediments from detrital sources. The remaining P burial must therefore be a result of export production from marine surface waters (Filippelli et al., 2007). Molybdenum is believed to serve as a proxy for deposition under euxinic conditions in marine bottom waters (e.g., Meyers et al., 2005). There is little observed variation in P_{tot}/Ti in the HSM. At the onset of OAE 2 there is a noticeable decline in this ratio followed by an increase to the highest observed values in the section in the upper BCL (Fig. 3.4). These higher values coincide with the decline in P_{det} accumulation rates to near zero (Fig. 3.3). Molybdenum concentrations are highest in the HSM and lowest in the lower BCL during the earliest stages of OAE 2. Mo levels increase during the latter portions of OAE 2 and ultimately reach a peak value for the BCL immediately following OAE 2. The intervals characterized by elevated concentrations of Mo coincide with the highest values of C_{org}/P_{react} while lower Mo concentrations are coincident with lower ratio values (Fig. 3.4).

Lastly for deposits of the USGS #1 Portland core, comparisons between P accumulation and detrital proxies including Ti/Al , Na/K , and $K/(Fe+Mg)$ (elemental

Figure 3.4. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$, P accumulation rates, $\text{C}_{\text{org}}/\text{P}_{\text{react}}$, $\text{P}_{\text{tot}}/\text{Ti}$, and Mo concentration data for the HSM and BCL in the USGS #1 Portland Core. $\delta^{13}\text{C}_{\text{org}}$ as well as C_{org} , Ti, and Mo concentration data were obtained from previously published results (Pratt, 1993; Sageman and Lyons, 2003; Sageman et al., 2006; Sageman et al., 1997; Sageman et al., 1998).

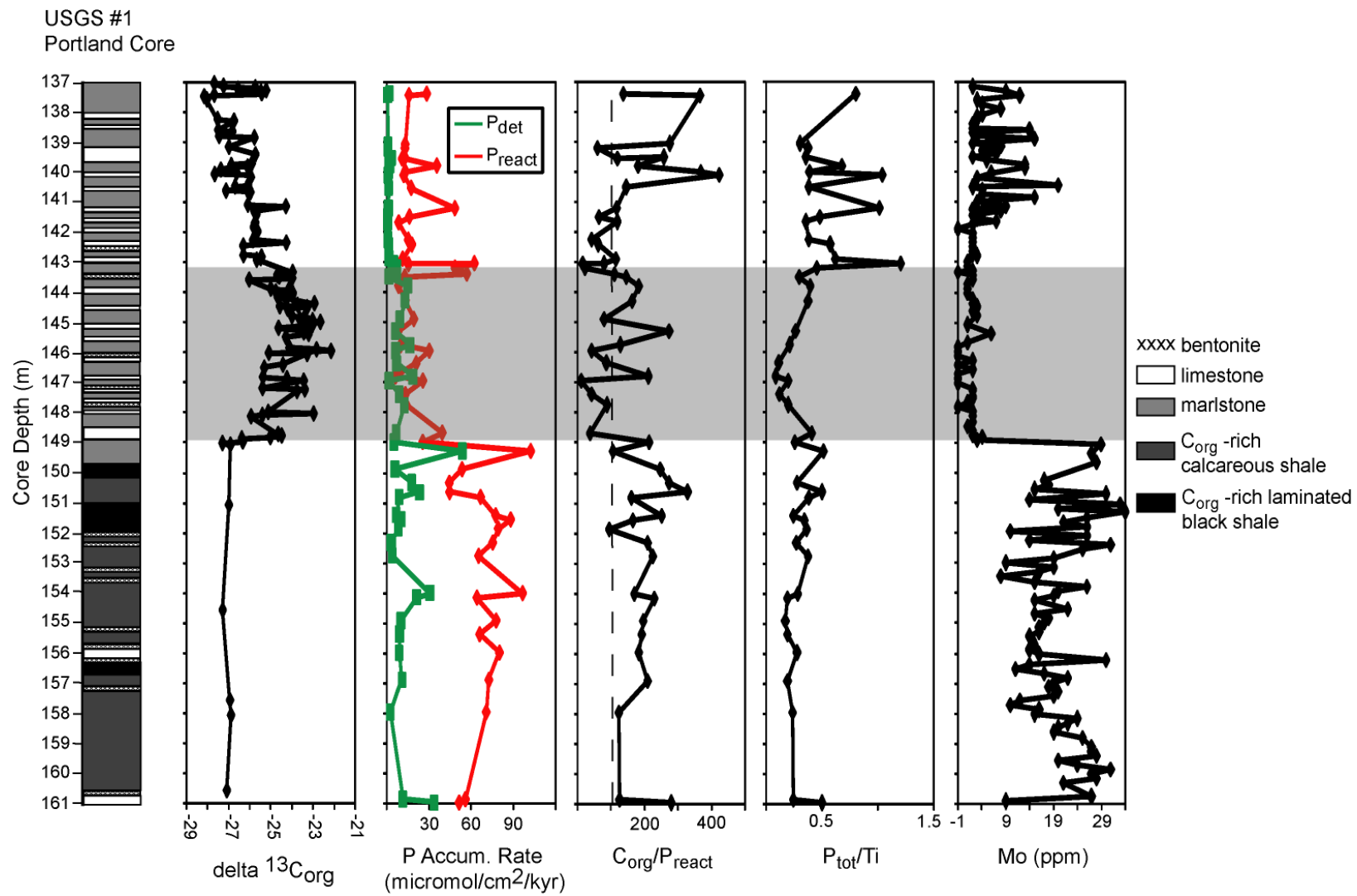


Figure 3.4.

Figure 3.5. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$, P accumulation rates, and detrital proxies Ti/Al, Na/K, and K/(Fe+Mg) for the HSM and BCL in the USGS #1 Portland Core. $\delta^{13}\text{C}_{\text{org}}$ as well as trace element data were obtained from previously published results (Pratt, 1993; Sageman and Lyons, 2003; Sageman et al., 2006; Sageman et al., 1997; Sageman et al., 1998).

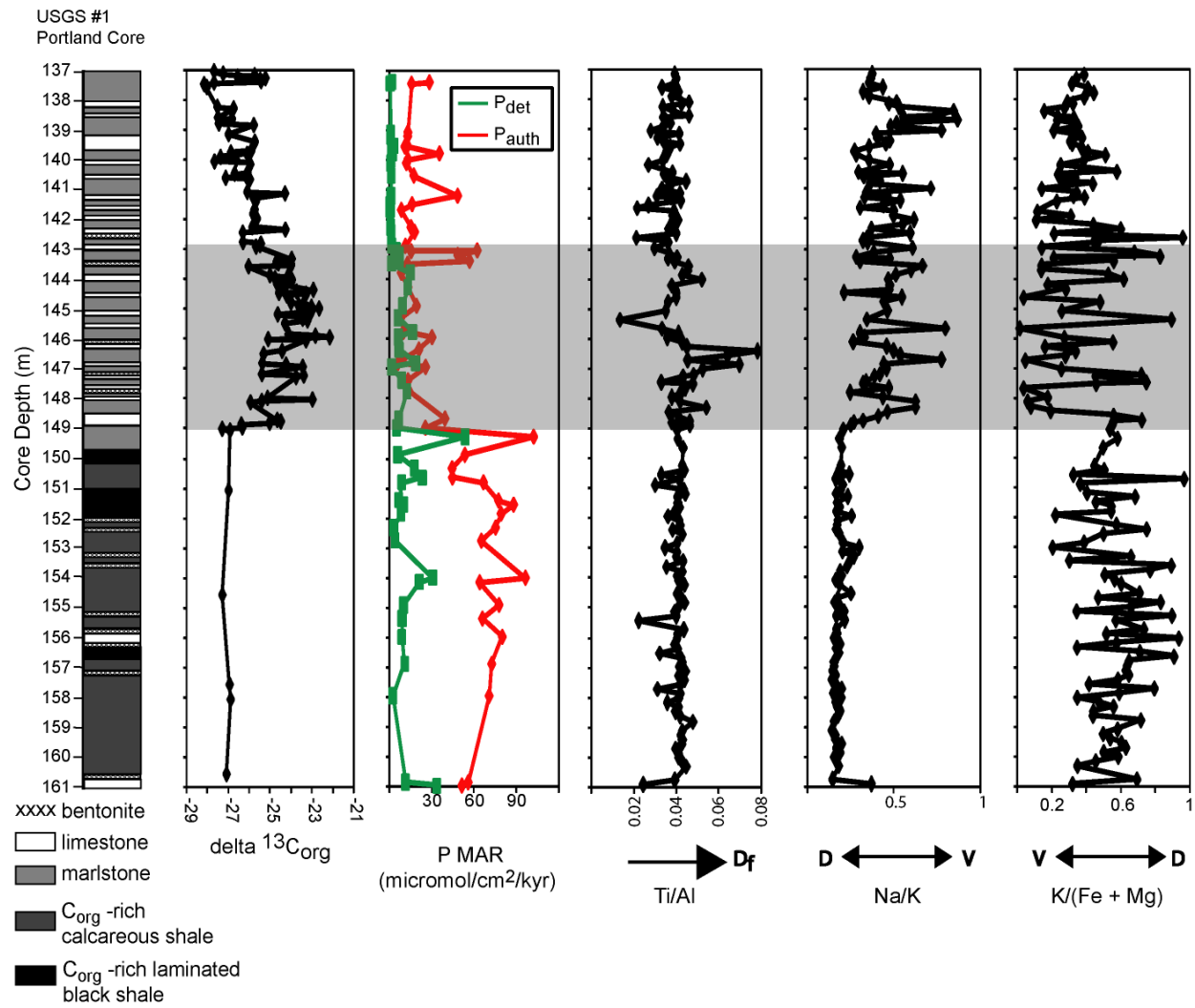


Figure 3.5.

concentrations from Sageman et al., 1997 and 1998; Sageman and Lyons, 2003) are made (Fig. 3.5). As demonstrated in Chapter 2, such comparisons can be utilized as a proxy for riverine P input to marine surface waters. Observed detrital input is greatest in deposits of the HSM (as characterized by low Na/K and K/(Fe + Mg) ratios, greater bulk MAR, and P_{det} MAR) (Fig. 3.5), which would be expected during a time of lower sea-level. A plot of bulk MAR vs. P_{det} concentration for the BCL provides final support for this hypothesis (Fig. 3.6). The observed trend of increased P_{det} with greater bulk MAR provides strong supporting evidence that variations in P_{det} concentration can be utilized as a proxy for relative changes in the flux of terrestrially derived nutrients to marine surface waters.

4.3.2 Ram Falls

Concentration data for C_{org} , P, and $C_{\text{org}}/P_{\text{react}}$ at this section are presented in Appendix 2 and Figure 3.6. Organic C concentrations range between 0.7 and 3.04 wt. %. Two increasing trends are observed in the section. Values increase from a low of 0.77 wt. % at the bottom of the section analyzed to 2.65 wt. % immediately prior to the onset of the event (a 71% increase). There is then a 48% decrease in concentration during the earliest stages of OAE 2 to 1.37 wt. % followed by another increase to peak values of 3.04 wt. % following OAE 2. Concentrations of P_{react} demonstrate a very similar trend with values increasing from 17.7 $\mu\text{mol/g}$ to 21.6 $\mu\text{mol/g}$ immediately preceding the event, falling to 13.4 $\mu\text{mol/g}$ during OAE 2, and then rising again to peak values of 28.2 after the event. There is less variation in P_{det} through the section, predominantly ranging between 3.8 and 9.5 $\mu\text{mol/g}$ with a minimal increasing

Figure 3.6. Cross plot of bulk MAR (Sageman et al., 2006) vs. P_{det} concentrations for samples of the BCL analyzed in this study. The trend of increasing P_{det} with increasing bulk MAR lends strong supporting evidence to the hypothesis that variations in P_{det} can serve as a proxy for relative changes in the flux of terrestrially derived nutrients to marine surface waters.

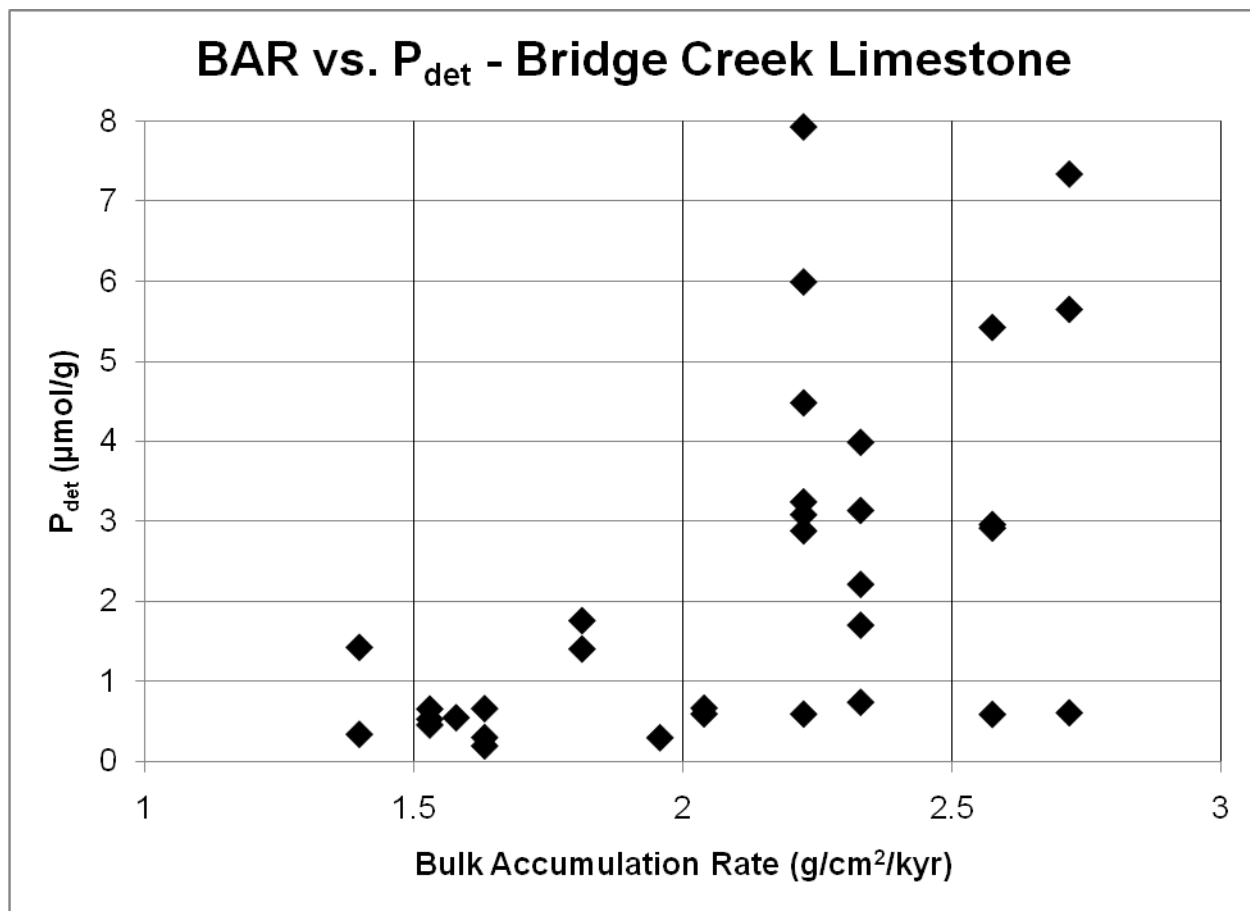


Figure 3.6.

trend before the event and subsequent decrease following it. A peak value of 18.2 $\mu\text{mol/g}$ is observed in a mudstone interval containing thin beds of very fine to fine grained sandstones in the lowermost portion of OAE 2 (Fig. 3.7).

Accumulation rates of P and C are demonstrated in Figure. 3.8 and are given in Table 3.2. Over the 9 m interval prior to OAE 2 P_{react} accumulation rates demonstrate little variation ranging between 24 – 29 $\mu\text{mol/cm}^2/\text{kyr}$. However, P_{det} accumulation rates during the same interval show an increasing trend up section from 5 – 12 $\mu\text{mol/cm}^2/\text{kyr}$. Within the OAE 2 interval P_{react} values initially decrease to the lowest value recorded in the section (19 $\mu\text{mol/cm}^2/\text{kyr}$) but quickly return to pre-event values in the latter half of the interval. With the exception of an increased value in the very fine to fine grained sandstone unit, P_{det} accumulation rates remain fairly consistent with pre-event values throughout OAE 2. Following OAE 2, P_{react} rates again increase reaching the highest values achieved in the section (up to 34 $\mu\text{mol/cm}^2/\text{kyr}$) while P_{det} decreases to values similar to those preceding the increase prior to the onset of OAE 2 (4 – 13 $\mu\text{mol/cm}^2/\text{kyr}$).

The range of P_{react} accumulation rates observed here are similar to those of modern outer continental shelf to basinal marine environments (Cha et al., 2005; Slomp et al., 1996a), and match those observed in the BCL at the USGS #1 Portland Core Site (Table 3.2). However, the P_{det} accumulation rates observed at this locale are much more similar to those of the HSM in central CO, suggesting a shallower setting with higher terrigenous inputs. This interpretation is consistent with the occurrence of silt

Figure 3.7. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$, C_{org} , CaCO_3 , and P concentrations, and $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ ratios for the Ram Falls outcrop section across the OAE 2 interval. The dashed line on the $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ plot represents the Redfield value of 106:1. The shaded interval highlights deposits of OAE 2.

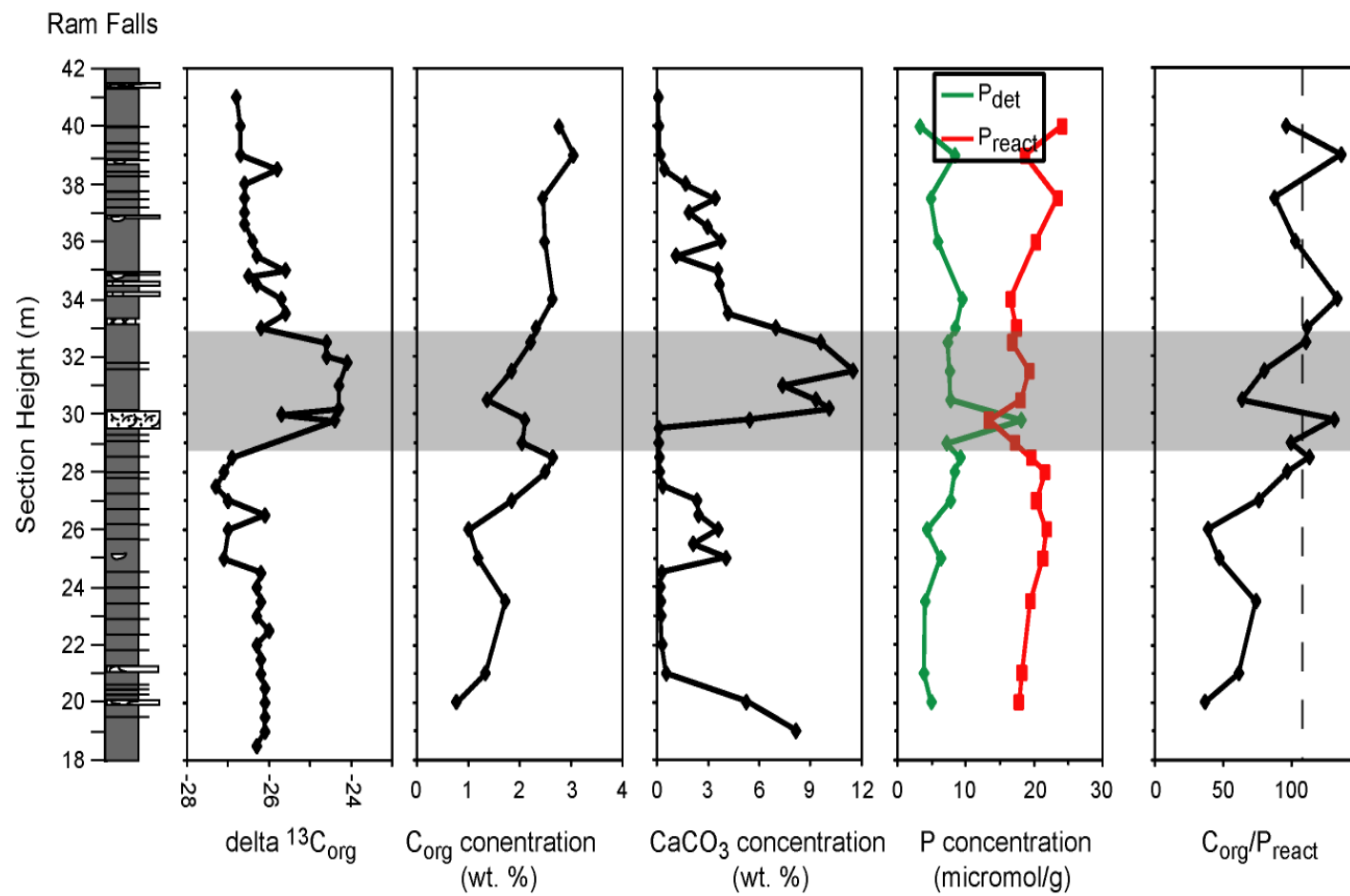


Figure 3.7.

Figure 3.8. Accumulation rates of C_{org} , $CaCO_3$, and P at the Ram Falls outcrop section. Sedimentation rates (0.67 cm/kyr) and bulk accumulation rates (1.34 g/cm²/kyr) are assumed constant throughout the OAE 2 interval at this site.

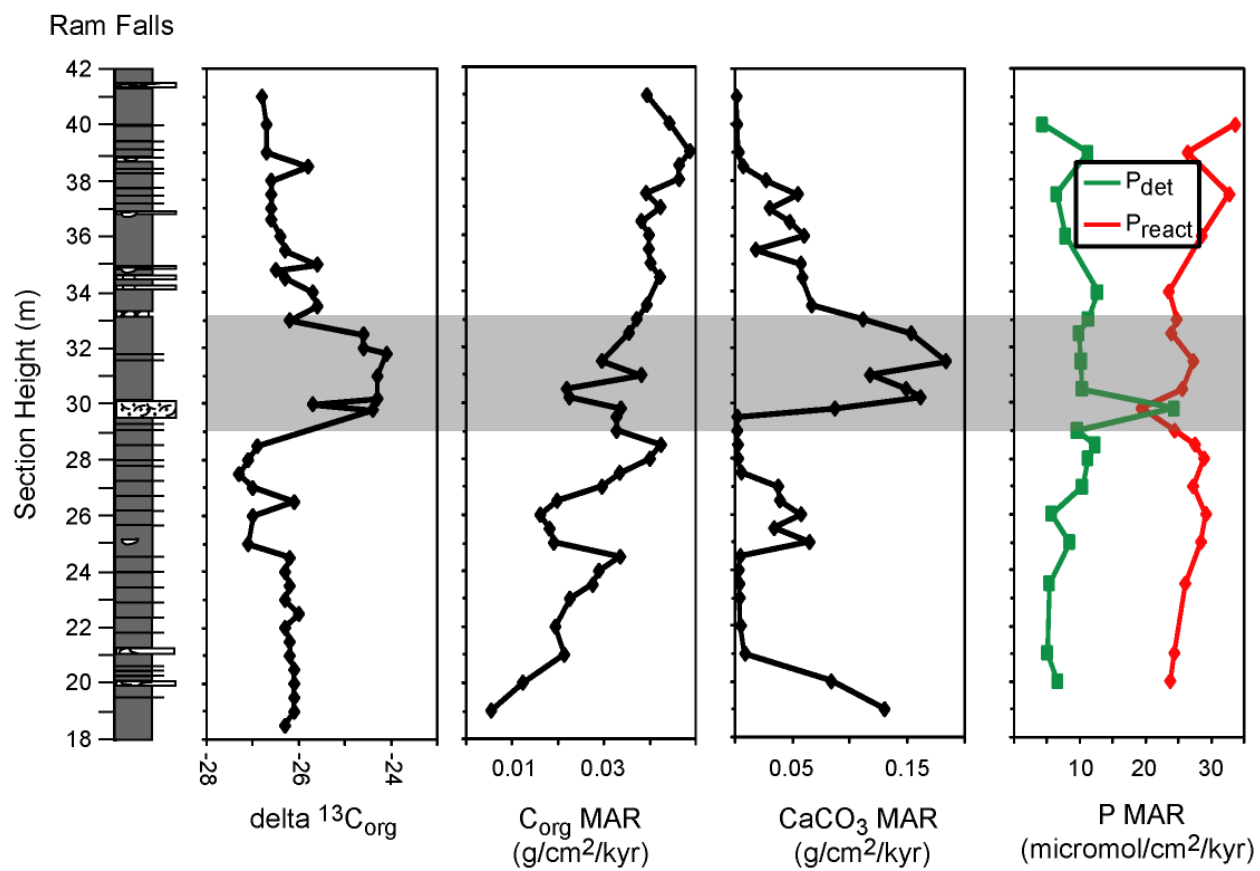


Figure 3.8

facies throughout the section, relatively low C_{org} and $CaCO_3$ concentrations (Fig. 3.7) and deposition in a higher latitude / higher precipitation environment.

Values of C_{org}/P_{react} are generally less than Redfield leading up to the onset of OAE 2 (Fig. 3.7). With the exception of two samples within the OAE, most values during and following the $\delta^{13}C$ excursion are slightly greater than Redfield. In the section preceding OAE 2 average values are 68, during OAE 2 they are 99, and following OAE 2 they are 111. These low values are consistent with deposition in a shallow marine environment with relatively high sedimentation rates (Ingall and Van Cappellen, 1990). Some potential changes in the chemical characteristics of the water column through the OAE 2 interval are indicated by the general increasing trend of the C_{org}/P_{react} ratio as well as the accumulation of redox sensitive trace elements such as Mo at a nearby site during the latter stages of the OAE 2 interval (Sageman, personal communication).

3.3.3 ODP Site 1258

Concentration data for P and C from ODP Site 1258 are given in Appendix III and demonstrated in Figure 3.8. Organic C concentrations are high throughout the interval ranging between 3.16 – 28.6 wt. % (Erbacher et al., 2005). The lowest concentrations occur in the limestone facies whereas the highest are in the laminated black shales in OAE 2 (Fig. 3.8). Carbonate concentrations are variable throughout the section ranging from values near zero in the C_{org} –rich black shales of OAE 2 to values greater than 90 wt. % in limestone facies (Fig. 3.9).

Figure 3.9. Lithologic log, $\delta^{13}\text{C}_{\text{org}}$, and C_{org} , CaCO_3 , and P concentrations for ODP Site 1258. Lithologic descriptions were obtained from Erbacher et al. (2004) while $\delta^{13}\text{C}_{\text{org}}$ and C_{org} concentrations are also from previously published results (Erbacher et al., 2005).

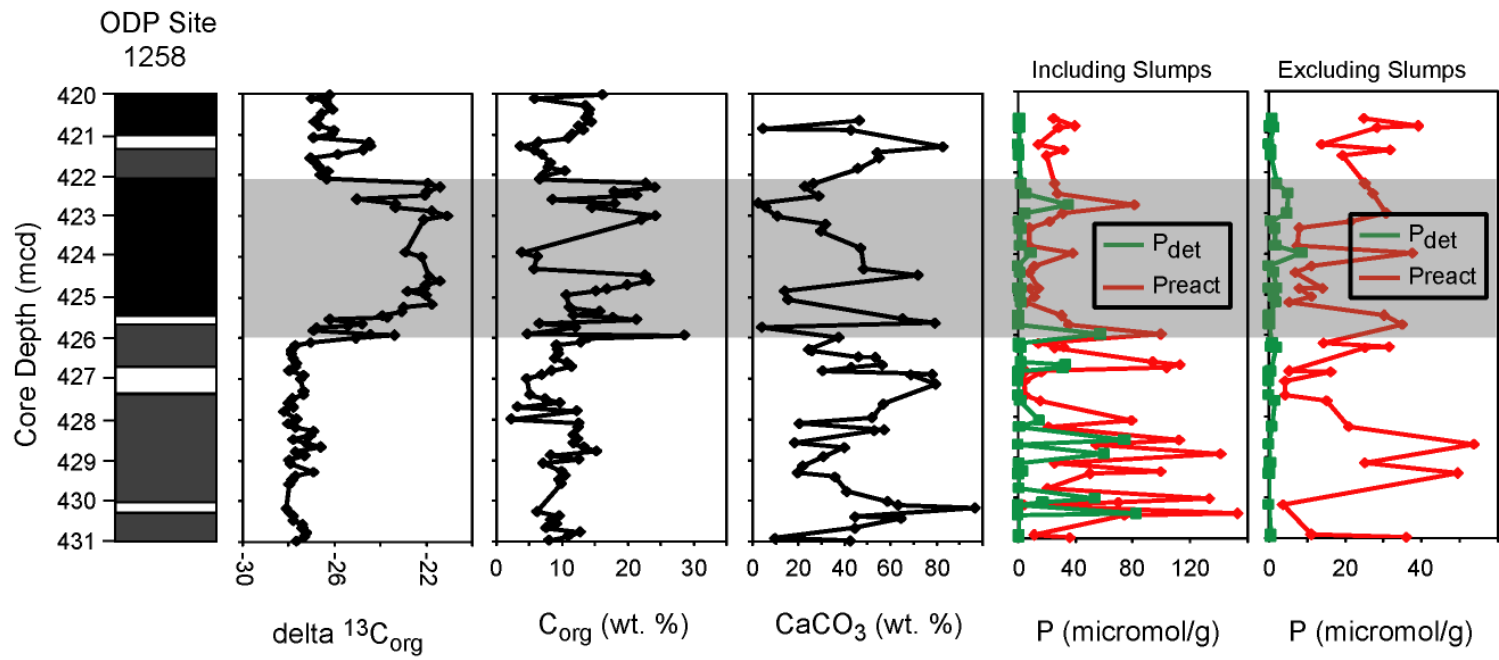


Figure 3.9.

Significant variation is observed in the P concentration data for both P_{det} and P_{react} phases throughout the study interval at this site (Fig. 3.9). This is a surprising observation considering that this site is interpreted to represent middle to upper bathyal water depths during C – T time (Erbacher et al., 2004) and therefore should have been far removed from any significant detrital input. However, comparison of the samples for which increases in both the P_{det} and P_{react} concentrations occur to on-board core descriptions (Erbacher et al., 2004) at the same depths indicate that such deposits may be associated with winnowing of pelagic muds due to gravity flow or current processes. Such processes may have concentrated P –rich fish debris and other P_{react} phases to abundances sufficient to supersaturate the step of the SEDEX method designed to measure them (see Chapter 2 for further details of this hypothesis). Because such deposits do not represent normal hemipelagic to pelagic marine sedimentation, they are not included in the analysis of the marine P cycle at this locale during the OAE 2 interval.

Analysis of P_{react} concentrations in sediments not associated with winnowing demonstrates a fairly consistent association with lithology (Fig. 3.9). Highest concentrations occur in the less C_{org} -rich gray shales and lowest in the highly C_{org} -rich laminated black shales and limestone facies. This implies more efficient retention of P released during OM degradation in the gray shales versus the laminated black shales consistent with an effective Fe-oxyhydroxide trap in marine bottom and pore waters during such intervals (Slomp et al., 2004; Slomp and Van Cappellen, 2007).

Figure 3.10. Lithologic log (Erbacher et al., 2004), $\delta^{13}\text{C}_{\text{org}}$ (Erbacher et al., 2005) bulk mass accumulation rate, and C_{org} , CaCO_3 , and P accumulation rates for C – T deposits at ODP Site 1258. Sedimentation rates to calculate the bulk accumulation rate are taken from the timescale of OAE 2 derived by Sageman et al. (2006) while dry bulk densities were obtained from previously published GRA measurements (Erbacher et al., 2004). C_{org} concentrations used to calculate accumulation rates were obtained from Erbacher et al. (2005).

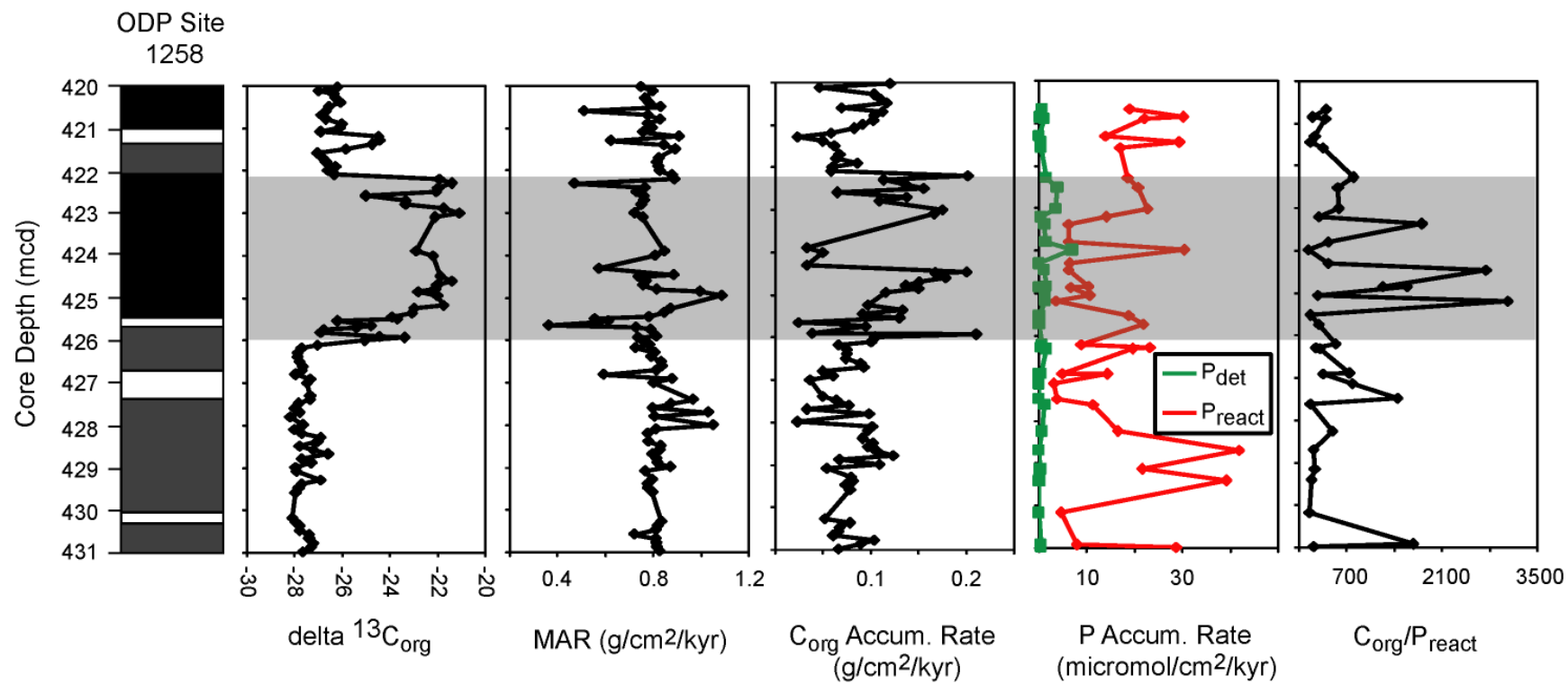


Figure 3.10.

Detrital P concentrations in the non-winnowed deposits are at or near zero throughout (Fig. 3.9), as would be expected for this oceanic hemipelagic – pelagic environment.

Accumulation rates vary through the section in part due to variations in the dry bulk density values (Erbacher et al., 2004). Figure 3.10 shows the bulk MAR through the interval along with MAR values for C_{org} , $CaCO_3$, and P. Average C_{org} accumulation rates are greatest in the black shales of OAE 2 ($0.14 \text{ g/cm}^2/\text{kyr}$) while in shale and carbonate facies not associated with OAE 2 such accumulation rates average $0.09 \text{ g/cm}^2/\text{kyr}$, thus demonstrating a 36% increase in C_{org} accumulation during OAE 2 at this site. Reactive P accumulation rates average $26 \text{ } \mu\text{mol/cm}^2/\text{kyr}$ in the gray shale facies proceeding and following OAE 2, while average values in the C_{org} –rich black shales deposited during the event and the limestone facies are 15 and $9 \text{ } \mu\text{mol/cm}^2/\text{kyr}$, respectively. Assuming the shale facies as representing the predominant depositional environments at this site, there is a 42 % decline in P_{react} accumulation during OAE 2 relative to before and after the event. All of the P_{react} accumulation rates observed here are consistent with deposition in a basinal marine setting when compared to modern values (Cha et al., 2005) (Table 3.2).

Values for C_{org}/P_{react} demonstrate significant variability throughout the section (Fig. 3.10). However, the highest values all occur within the OAE 2 interval; nearly all of these values are much greater than Redfield. Average values in the C_{org} –rich black shales within OAE 2 are 1022 and range between 137 – 3068 with the greatest value immediately following the initiation of the event and the lowest values in the interval of low C_{org} concentrations around 424 mcd (Fig. 3.10). In the less C_{org} –rich shales and

carbonate facies preceding and following OAE 2 average C_{org}/P_{react} values are 452 and range between 155 and 1675. Based on observations in the KWIS, such values at this locale suggest that these deposits formed under a low sedimentation rate with varying redox conditions in marine bottom and pore waters. This is consistent with previous interpretations of middle to upper bathyal water depths at this site during C – T time (Erbacher et al., 2004) and possible intervals of water column euxinia based on the observation of isorenieratane within some of the black shale facies at a nearby DSDP Site (Kuypers et al., 2002).

3.4 DISCUSSION

3.4.1 KWIS

Geochemical data from both the USGS #1 Portland Core and Ram Falls outcrop sections indicate enhanced P_{det} accumulation prior to the onset of OAE 2. These observations are consistent with previously published proxies of enhanced detrital input during deposition of the HSM based on trends in Na/K and K/(Fe +Mg) ratios (Sageman and Lyons, 2003; Sageman et al., 1997; Sageman et al., 1998) and similar evidence in deposits from the Ribstone core, which was drilled to the east of the Ram Falls outcrop section (Sageman, personal communication). At each site, P_{det} accumulation decreases throughout the OAE 2 interval to minimal observed values at the end of the event and throughout the post-OAE 2 interval. These trends are consistent with previously published observations supporting rising sea-level throughout the interval culminating in a highstand at the end of the $\delta^{13}\text{C}$ excursion (Arthur and Sageman, 2005; Laurin et al., 2005; Laurin and Sageman, 2001).

Increased detrital input, with peak values immediately prior to the onset of the event, is consistent with recently published work indicating enhanced chemical weathering at the same time interval (Frijia and Parente, 2008). In their study, Frijia and Parente (2008) compiled a high resolution $^{87}\text{Sr}/^{86}\text{Sr}$ isotope curve across the OAE 2 interval and observed peak values, indicating enhanced continental runoff, straddling the onset of the event. Potential mechanisms to explain such an increase in chemical weathering will be explained in the subsequent section. However, these observations provide further supporting evidence that the observed increased P_{det} accumulation

preceding the onset of OAE 2 was related to an overall increase in the flux of terrestrially derived material to the marine realm, including bioavailable P.

It has been interpreted that bottom and pore waters at the Portland Core site were relatively oxic at the onset of OAE 2 (Meyers et al., 2005; Savrda, 1998). This interpretation is based on observations of extensive bioturbation (Savrda, 1998) and a decline in the concentration of redox sensitive trace elements such as molybdenum (Meyers et al., 2005). Such interpretations are counterintuitive during an interval characterized by global anoxia in the open ocean. However, water depth estimates of Sageman and Arthur (1994) provide minimum estimates of ~175 m in the deepest parts of the basin during the maximum sea-level highstand. Increasingly, evidence suggests that such depths may have been as low as 100 – 150 m and thus, following the initial transgression at the onset of OAE 2, the basin may have been well mixed, thus preventing permanent stratification and bottom water anoxia.

In this study observations of low C_{org} and C_{org}/P_{react} ratios below Redfield provide further evidence to support interpretations of an oxic basin during OAE 2. The lowest ratio values at the Portland Core site are observed in the lower BCL, while at the Ram Falls section they are at or less than Redfield throughout the interval, except for some slightly elevated values following the event. The low C_{org}/P_{react} values in the lower BCL can be explained by the dominance of oxic respiration as the main mechanism of OM degradation during deposition of this unit. Such processes have been observed in modern environments to result in the lowest preservation of C_{org} , but the greatest retention of P_{react} in surficial marine sediments (Anderson et al., 2001; Ruttenberg and

Goni, 1997; Slomp et al., 1996a; Slomp et al., 1998). In deposits of the lower BCL, the interpretation of low C_{org} accumulation under oxic conditions can be supported (Fig. 3.3). However, contrary to modern observations, there is also a decline in P_{react} accumulation during this time (Fig. 5.3). Potential mechanisms to explain this, in particular the role of iron, will be discussed further in Chapter 4.

3.4.2 ODP Site 1258

As would be expected in deposits from a hemipelagic to pelagic marine environment deposited in middle to upper bathyal water depths, there is little to no accumulation of P_{det} at ODP Site 1258. Thus, terrigenous input should not have been the primary source of nutrients to surface waters at this site during the OAE 2 interval.

Overall, C_{org}/P_{react} ratios are well above Redfield throughout the entire section at this site. This suggests a prominence of oxygen-deficient conditions even before the onset of OAE 2. However, during the event, ratio values are extreme, especially in the early stages, with values greater than 3000 (Fig. 3.10). These observations are similar to those from previous studies which demonstrated increased $(C/P)_{org}$ and C_{org}/P_{react} values across a range of depositional environments in the global ocean during OAE 2 (Mort et al., 2007; Nederbragt et al., 2004). Thus, observations from this and previous studies indicate that increased regeneration of P under oxygen-deficient conditions in the open ocean had a role in maintaining the increased flux of nutrients to marine surface waters necessary for the interpreted increased rates of production during OAE 2.

3.4.3 Conceptual Model

Utilization of SEDEX across the range of environments analyzed in this study allows for the direct assessment of two of the previously hypothesized causal mechanisms of an enhanced nutrient flux to marine surface waters during the OAE 2 interval: 1) greater regeneration of P under oxygen – deficient conditions (Mort et al., 2007; Nederbragt et al., 2004) and 2) a greater flux of terrestrially derived nutrients due to greater rates of chemical weathering (Erbacher et al., 1996; Frijia and Parente, 2008; Weissert, 1989). Examination of the P cycle in deposits of the KWIS indicates greater deposition of P_{det} mineral phases prior to the onset of the event with peak accumulation immediately preceding initiation of the $\delta^{13}\text{C}$ excursion. Observations at ODP Site 1258 suggest greater nutrient regeneration during the event in the open ocean. Thus, it is demonstrated here that both mechanisms were important in the initiation and maintenance of OAE 2. However, other mechanisms must also be invoked to provide the climatic conditions necessary for increased rates of chemical weathering, to bring the nutrients released during OM degradation in the open ocean back to the photic zone, and to provide additional sources of nutrients unable to be accounted for in this study.

The OAE 2 interval has widely been recognized as one of extreme warmth (Forster et al., 2007; Huber et al., 2002; Schouten et al., 2003) with $p\text{CO}_2$ estimates of 4 to 6 times pre-industrial averages (Arthur et al., 1985; Berner and Kothavala, 2001; Bice and Norris, 2002). Such high temperatures and CO_2 concentrations must have been the result of greater volcanic and hydrothermal activity, which has also been postulated

as both a causal factor of the event itself and as a potential source of micro-nutrients such as iron (Sinton and Duncan, 1997; Snow et al., 2005; Turgeon and Creaser, 2008). In particular, Turgeon and Creaser (2008) have suggested that increased volcanism initiated the event, based on observations of changes in osmium isotopic ratios and concentrations, within 23 kyr of the onset of the event. The possibility of increased global volcanism prior to the OAE 2 onset suggests the hypothesis that CO₂ – fueled warming intensified the hydrologic cycle, increased rates of chemical weathering, and resulted in higher fluxes of dissolved P to the marine realm, as also suggested by Sr isotopic evidence (Frijia and Parente, 2008).

An additional hypothesis regarding potential nutrient sources to marine surface waters during OAE 2 argues for increased upwelling due to changes in circulation patterns in the global ocean. Two potential mechanisms have been proposed for such a change in upwelling: 1) a rise in global sea-level (Arthur et al., 1987) and 2) opening of the gateway between the North and South Atlantic Oceans (Summerhayes, 1987). Although exploring the mechanisms controlling rates of upwelling during the OAE 2 interval is outside the scope of this study, such processes would have had to be significant during the event in order to return the P released by OM degradation to the photic zone to fuel further primary production.

A final mechanism that has recently been invoked to provide an additional nutrient flux to marine surface waters during OAE 2 is the potential release of P from shallow marine sediments following a sea-level rise event (Bjerrum et al., 2006). Such a mechanism is similar to that invoked in the shelf – nutrient hypothesis to explain

increased rates of primary production at the end of glacial cycles during the Pleistocene (Filippelli et al., 2007). Although the modeling study of Bjerrum et al. (2006) concluded that such P release could not increase productivity sufficiently to explain the full $\delta^{13}\text{C}$ excursion of OAE 2, the timing of the sea-level rise at the onset of the event suggests that such P release may have been an additional source of bioavailable nutrients.

In summary, a plausible consensus hypothesis for the initiation of OAE 2 invokes increased chemical weathering due to volcanic –sourced CO_2 resulting in an elevated flux of terrestrially derived nutrients to marine surface waters. The resulting increased productivity, along with increased hydrothermal activity, caused expansion of the OMZ throughout the global ocean. At the onset of the event marine bottom and pore waters were sufficiently oxygen-deficient in many areas to result in preferential release of P during OM degradation processes. Phosphorus produced by this process, combined with P from enhanced upwelling, possibly related to global sea-level rise or opening of the gateway between the North and South Atlantic Oceans, as well as P released from shallow marine sediments during a sea-level rise, resulted in enhanced production, widespread oxygen deficiency, and development of a productivity – anoxia feedback which sustained the flux of nutrients to marine surface waters for the duration of the event.

3.5 CONCLUSIONS

Previous studies of potential nutrient sources to marine surface waters during OAE 2 have primarily focused on individual mechanisms. Such studies have resulted in numerous working hypotheses. This study utilized the SEDEX sequential extraction procedure to directly examine the hypotheses of increased terrestrially sourced P and enhanced regeneration of P during OM degradation under oxygen-deficient conditions. Results indicate that both processes were occurring and lead to a conceptual model taking into account several working hypotheses acting together to explain many of the geochemical observations that characterize this and other studies of the C – T interval. A reasonable mechanism for the cessation of the event is still lacking. From observations summarized here, one possible mechanism could be increased oxygenation of the atmosphere resulting from enhanced primary production and mixing with marine surface waters and subsequent oxidation of bottom and pore waters during oceanic overturn (VanCappellen and Ingall, 1996).

CHAPTER 4

MODELING OF THE PHOSPHORUS BUDGET IN THE KWIS ACROSS THE OAE 2 INTERVAL

4.1 INTRODUCTION

As demonstrated in Chapter 3 of this dissertation, evaluation of the P budget (via geochemical techniques) in the Cretaceous Western Interior Seaway (KWIS) during the Cenomanian - Turonian (C-T) OAE 2 interval suggests that prior to the event there was an increased flux of terrestrially derived phosphorus (P) to the marine realm. At the onset of the event this flux is greatly diminished and becomes negligible following the event as indicated in deposits from the USGS #1 Portland Core. This is an expected trend considering interpretations of a significant sea-level transgression at the onset of the event (Arthur and Sageman, 2005; Laurin et al., 2005; Laurin and Sageman, 2001). However, considering published estimates of increased primary production and oxygenation of bottom and pore waters in the KWIS during the event (Meyers et al., 2005), it was surprising to observe a significant decrease in the accumulation of P_{react} phases (those considered to represent previously bioavailable P) as well at the onset of OAE 2 and lasting throughout the event (Fig 3.2).

Such interpretations of increased oxygenation are based upon observations of low concentrations of redox sensitive trace elements such as Mo (Meyers et al., 2005) and greater amounts of burrowing and larger burrow diameters in deposits representing OAE 2 in the lower Bridge Creek Limestone (BCL) (Savrda, 1998). These observations are in direct contrast to those of the Hartland Shale (HSM; the unit immediately

preceding the onset of OAE 2) and the upper BCL (immediately following OAE 2) which are characterized by significantly higher Mo concentrations and less burrowing (Meyers et al., 2005; Savrda, 1998). Thus, these intervals have been interpreted to have been deposited under more oxygen-deficient conditions, including possible water column euxinia (Meyers et al., 2005).

Based on the observations described above, one would expect enhanced P_{react} burial in early OAE 2 deposits of the KWIS with less efficient burial during deposition of the HSM and intervals of the BCL following OAE 2. Such expectations are based on observations in modern marine environments suggesting a significant role of iron oxides and oxyhydroxides in the sorption of dissolved P following release during organic matter (OM) degradation processes (Slomp et al., 1998; Slomp et al., 1996b). This sorption is believed to prevent P released from OM from being recycled back to the water column and eventually allows it to re-precipitate as a P_{auth} mineral phase such as carbonate fluorapatite (CFA) (Slomp et al., 1996a). However, when marine bottom waters become anoxic, the oxides and oxyhydroxides are reduced and no longer able to sorb dissolved P. Therefore, under such conditions, P released during OM degradation can be released back into the water column rather than precipitated in the sediment. Such conditions have been observed across a wide range of modern marine environments (Anderson et al., 2001; Babu and Nath, 2005; Filippelli, 2001; Ingall et al., 2005; Ruttenberg and Goni, 1997; Schenau and De Lange, 2001). Yet, rates of P_{react} burial across the OAE 2 interval in deposits from the USGS #1 Portland Core do not agree with these modern observations (Fig. 3.3).

This study pursues a preliminary modeling approach to attempt to simulate conditions that resulted in decreased burial of P_{react} in the more oxic facies of the lower BCL. Model parameters include basin dimensions (Sageman and Arthur, 1994), productivity estimates (Meyers et al., 2005), riverine input (Slingerland et al., 1996), average dissolved inorganic P (DIP) concentration in modern rivers (Meybeck, 1993), and P accumulation rate estimates from Chapter 3 of this study (Table 4.1). I utilize these parameters to ultimately predict the residence time and length of time to achieve steady state with regards to P in the sediment during deposition of the HSM, lower BCL (including OAE 2), and upper BCL (following OAE 2) intervals. Preliminary results are then compared to elemental geochemical data to provide possible hypotheses for the trends in P_{react} accumulation observed at this site.

TABLE 4.1- Model Parameters

Parameter	Description
k_{out}	Rate constant of water outflow from the basin. Equals the river input divided by the basin volume. It is assumed that inflow equals outflow and basin volume is constant.
MDIP	Mass of dissolved inorganic phosphorus within the water column. Equals the flux of phosphorus into the basin divided by the rate constant of the water outflow of the basin.
k_{sp}	Rate constant of phosphorus removal from water column. Equals the productivity flux times the basin area divided by the MDIP in grams.
k_{rp}	Rate constant of phosphorus regenerated from sediment. Equals the regeneration flux divided by the mass of phosphorus buried during deposition of the sediment layer.

Table 4.1. Descriptions of the model parameters calculated in this study.

4.2 MODEL PARAMETERS

A series of equations to ultimately determine the parameters described in Table 4.1 and the residence time of P in deposits of the HSM and BCL were derived from the steady state equation:

$$F_{in} + F_r = F_s + F_{out} \quad (4.1)$$

where F_{in} equals the flux of P into the basin from rivers, F_r equals the regeneration flux of P from OM degradation, F_s equals the sedimentation flux from previously calculated productivity rates, and F_{out} equals the flux out of the basin. These fluxes are demonstrated in Figure 4.1. From this equation and the assumption that $F_{in} = F_{out}$ equations for each of the fluxes can be derived.

$$F_s = k_{12}[DIP] \quad (4.2)$$

$$F_r = k_{21}[POP] \quad (4.3)$$

$$F_{out} = k_{1-out}[DIP] \quad (4.4)$$

From 4.1 – 4.4, a series of equations was derived and entered into a Microsoft Excel worksheet which calculated the rate constants and residence times of P in the two reservoirs shown in Figure 4.1. The initial equation utilized calculates the rate constant of water in the basin (k_{out}):

$$k_{out} = F_{rivers}/\text{basin vol.} \quad (4.5)$$

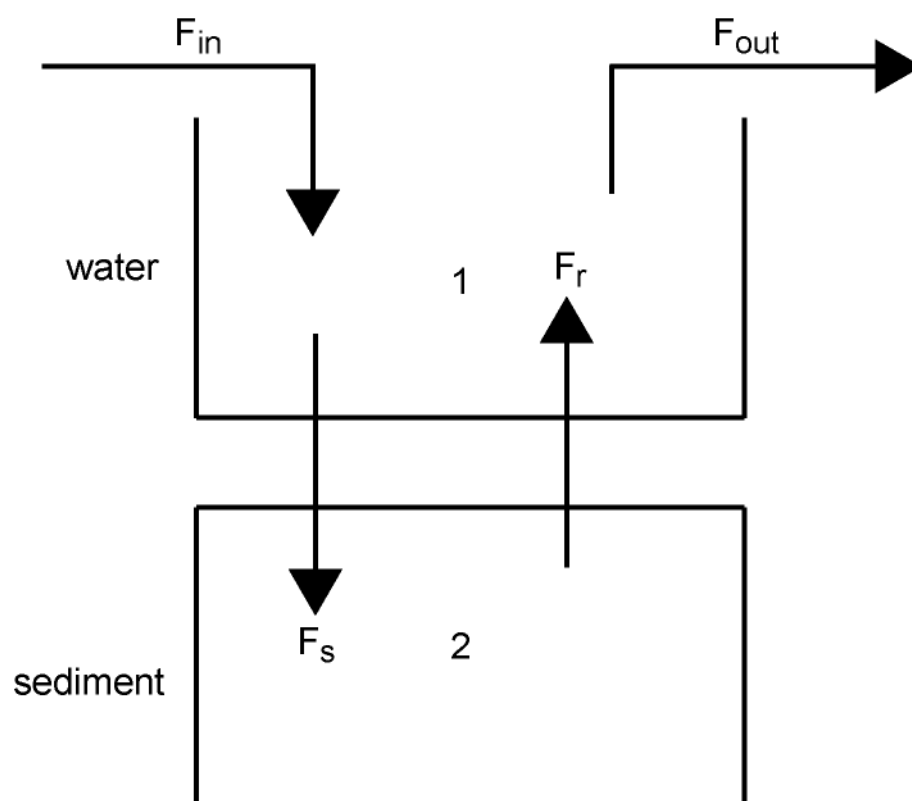


Figure 4.1. Schematic representing the fluxes calculated in equations 4.1 – 4.4.

This is considered constant throughout both the HSM and BCL intervals as the basin volumes and river input are assumed constant during each. In assuming a constant k_{out} , it is also assumed that the mass of DIP (MDIP) in the basin is constant. The equation to calculate MDIP is as follows:

$$MDIP = F_{in} / k_{out} \quad (4.6)$$

where F_{in} is the P input flux that is calculated as the product of river inflow and average concentration of DIP in modern unpolluted rivers (Meybeck, 1993). From MDIP it is then possible to calculate the rate constant of P in the water column (k_{sp}):

$$k_{sp} = (F_s * \text{basin area}) / MDIP \quad (4.7)$$

where F_s is calculated using previous productivity flux estimates of carbon (C) (Meyers et al., 2005) and assuming a Redfield ratio of 106:1 between C/P in OM. The rate constant of P regeneration in the sediment (k_{rp}) is the final parameter necessary to calculate the time to reach steady state in the basin:

$$k_{rp} = F_r / \text{mass P in sediment layer} \quad (4.8)$$

The rate constants as described above can be converted to calculations of residence time by taking the reciprocal of the rate constant. Residence times of P in the water column and sediment are given as the reciprocal of the rate constants:

$$RT_{water} = 1/k_{sp} \quad (4.9)$$

$$RT_{sed} = 1/k_{rp} \quad (4.10)$$

Steady state for the mass of P in sediment is defined as the average F_s divided by the average k_{rp} over a particular time interval. Such conditions were defined for three intervals during the C - T time: 1. pre-OAE 2 HSM; 2. OAE 2 BCL; and 3. post-OAE 2 BCL. For each interval, the equation used to calculate the mass of P in a sediment layer following the initiation of deposition of that layer is as follows:

$$\text{mass P} = (F_s / k_{rp}) * (1 - e^{-(k_{rp} * t)}) \quad (4.11)$$

where F_s is the average P flux to the sediment via organic matter and t is the amount of time following the initiation of a given interval. The t at which the mass P is equal to the steady state mass P is defined as the time necessary for an interval to reach steady state with regards to P in the sediment . These times are demonstrated for each of the intervals in this study in Figures 4.2, 4.3, and 4.4. A summary of each of the parameters discussed here is presented in Table 4.1.

Table 4.2 – Average Values of Model Parameters in C-T Intervals, Portland Core

Model Parameter	Avg. HSM	Avg. BCL (OAE 2)	Avg. BCL (post OAE 2)
$k_{sp} \text{ (yr}^{-1}\text{)}$	0.47	2.26	2.23
$k_{rp} \text{ (yr}^{-1}\text{)}$	0.0031	0.041	0.0441
residence time in water column (yr)	2.13	0.44	0.45
residence time in sediment (yr)	323	24	23

Table 4.2. Average values of the model parameters calculated in this study in the HSM and BCL intervals from deposits of the USGS #1 Portland Core.

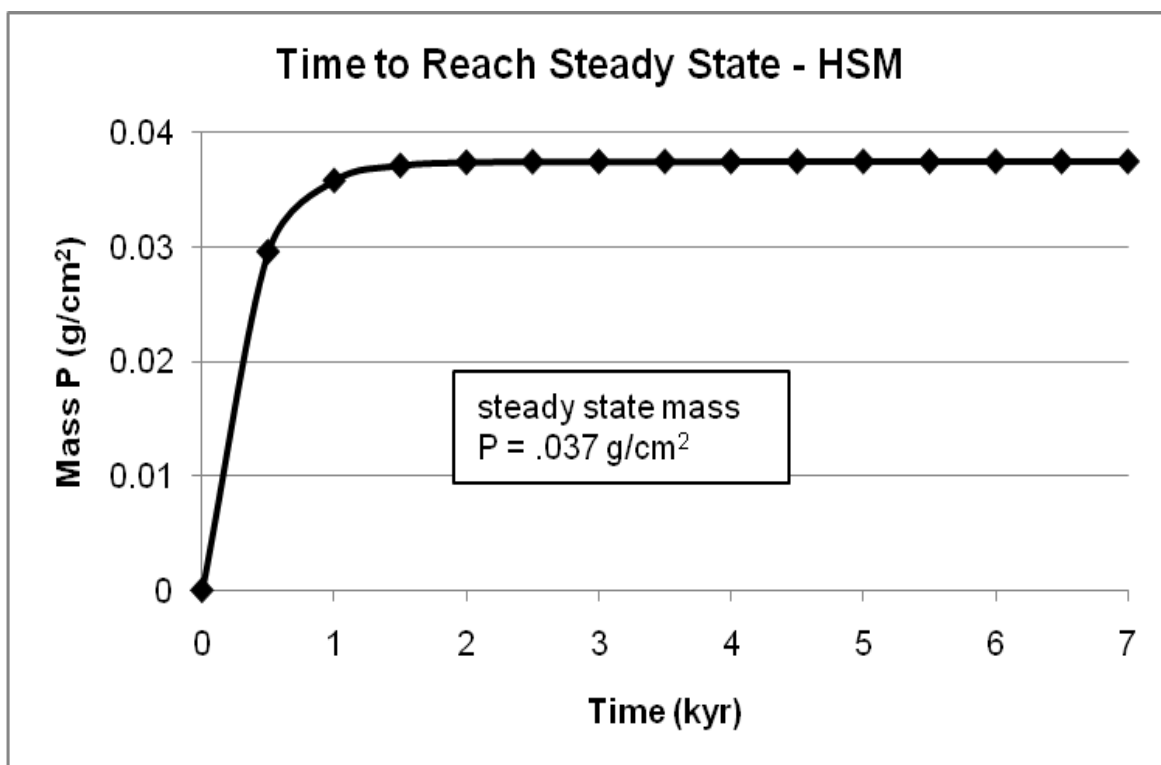


Figure 4.2. Plot of the mass P in the sediment versus time for the HSM. From this plot, steady state conditions were achieved in ~6 kyr during HSM deposition.

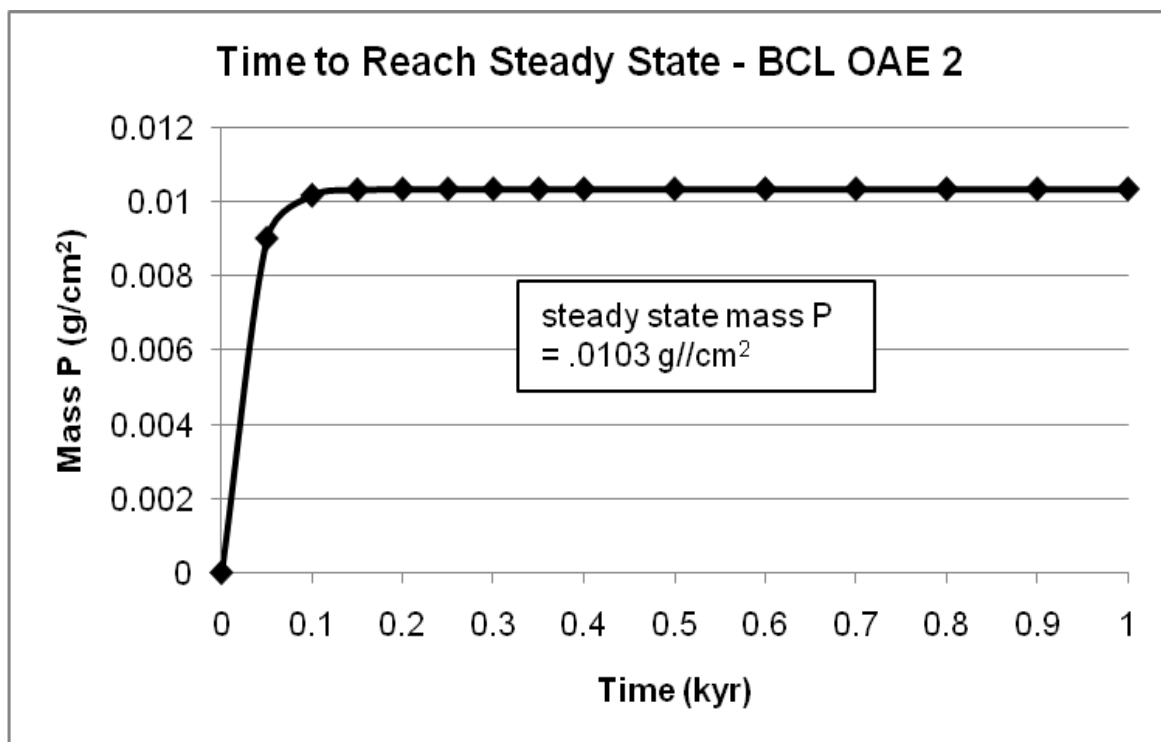


Figure 4.3. Plot of the mass P in the sediment versus time for the BCL during OAE 2. From this plot, steady state conditions were achieved in ~400 yr in this during this interval.

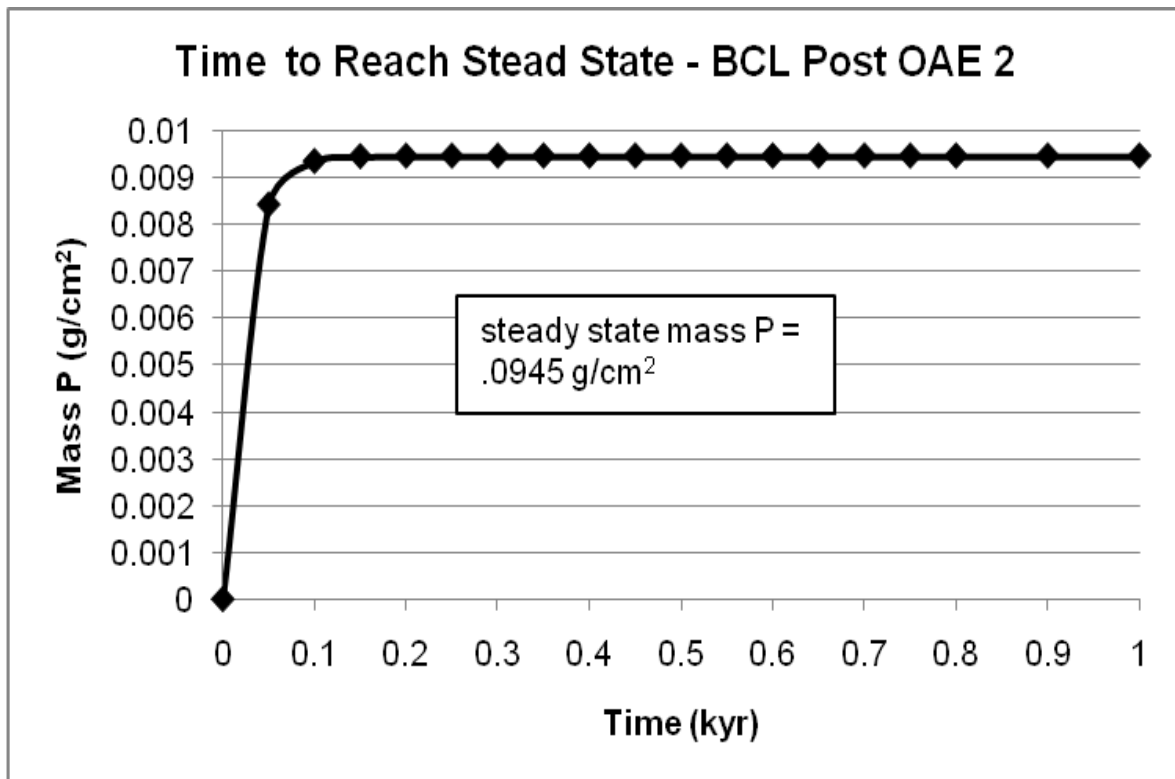


Figure 4.4. Plot of the mass P in the sediment versus time for the BCL following OAE 2. From this plot, steady state conditions were achieved in ~400 yr in this during this interval.

4.3 RESULTS

Rate constant calculations for water in the basin during the HSM and BCL intervals indicate very short residence times (~ 6 years for the HSM and 13 years for the BCL). Such short residence times are consistent with previous interpretations of rapid river input (Slingerland et al., 1996) into a shallow epicontinental seaway (Sageman and Arthur, 1994). K_{sp} calculations (Fig. 4.5) (avg. HSM = 0.47 yr^{-1} ; avg. BCL = 2.25 yr^{-1}) also indicate short residence times of dissolved P in the basin (~ 2 yr during HSM deposition; ~ 0.44 yr during BCL deposition). Such results are to be expected in a shallow marine basin with productivity rates ranging between modern Black Sea (during deposition of the HSM) and non-upwelling continental shelf environments (during deposition of the BCL) (Bralower and Thierstein, 1987).

Though slightly lower, k_{rp} calculations (Fig. 4.6) (avg. HSM = 0.003 yr^{-1} ; avg. OAE 2 BCL = 0.041 yr^{-1} ; avg. post-OAE 2 BCL = 0.044 ; Table 4.2) also indicate short residence times of P in sediments during these intervals (avg. HSM = 321 yr; avg. OAE 2 BCL = 24 yr.; avg. post-OAE 2 BCL = 23 yr.; Table 4.2). Low k_{rp} values result in calculations of short intervals of time necessary to reach steady state during each interval ($t = 6$ kyr during HSM; $t = 0.4$ kyr during OAE 2 BCL; $t = 0.4$ kyr during post-OAE 2 BCL; Table 4.2). Potential mechanisms controlling these low residence times and agreement with geochemical data collected during all intervals of this study is discussed in the following section.

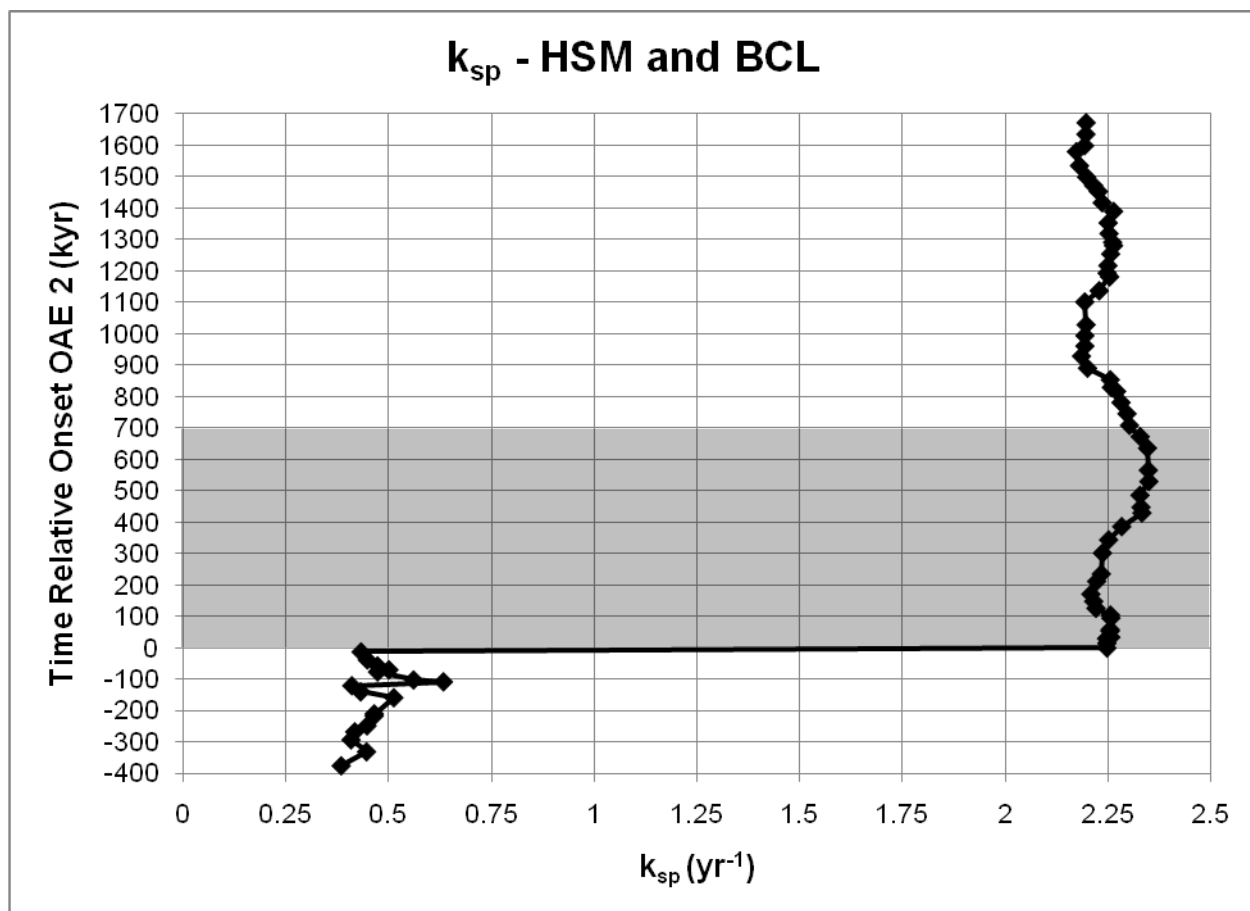


Figure 4.5. k_{sp} calculations for the HSM and BCL in deposits from the USGS #1 Portland Core. The HSM ranges from 0 - -400 kyr prior to the onset of OAE 2. The OAE 2 interval of the BCL ranges from 0 – 700 kyr relative to the onset of the event (demonstrated visually by the shaded section) while the post-OAE 2 interval ranges above 700 kyr after the onset and above.

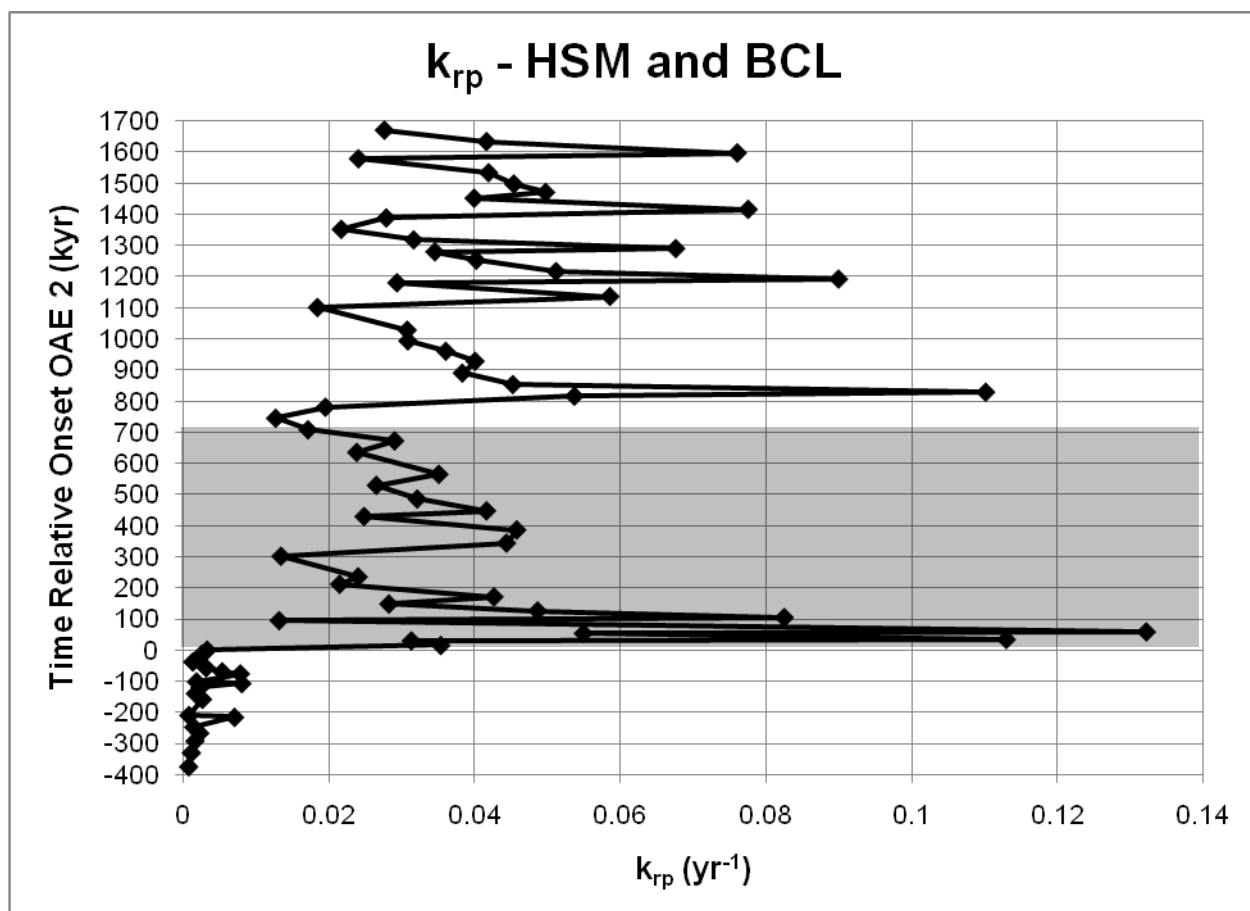


Figure 4.6. k_{rp} calculations for the HSM and BCL in deposits from the USGS #1 Portland Core. The HSM ranges from 0 - -400 kyr prior to the onset of OAE 2. The OAE 2 interval of the BCL (shown in the shaded region of the plot) ranges from 0 – 700 kyr relative to the onset of the event while the post-OAE 2 interval ranges from above 700 kyr after the onset and above. Calculations of an order of magnitude increase in the k_{rp} between the HSM and BCL suggest more efficient burial of P and a greater residence time of P in the sediments during the HSM.

4.4 DISCUSSION

Differences in residence time (and subsequently the time necessary to achieve steady state) calculations of P in HSM and BCL deposits presented in this study may indicate significant sedimentologic and geochemical variations in the water column and sediment during time of deposition. In particular, the residence time of P in HSM deposits is an order of magnitude greater than P in BCL deposits both during and following OAE 2. This is also reflected by an order of magnitude increase in the time necessary to achieve steady state P concentrations in deposits of the HSM versus those of the BCL. These calculations agree well with P geochemical data presented in Chapter 3 of this dissertation which demonstrate greater concentrations and accumulation rates of P during the HSM interval.

Before addressing factors associated with sedimentation in the basin, the possible saturation state of the waters with respect to CFA in both the HSM and BCL should be addressed. If the HSM was supersaturated with respect to CFA but the BCL not, there may have been water column precipitation of such mineral phases and thus greater accumulation. However, a recent study suggests that brackish water from the Baltic Sea is saturated with respect to such minerals but water column precipitation is prevented due to the presence of Mg^{2+} in the water column (Gunnars et al., 2004). It is further speculated by these authors that all seawater would have the same conditions. Though a percent saturation of the waters is not given, calculations of the saturation ratio in all samples analyzed (ranging between 1.1 to 7.5) indicate saturation with respect to CFA in their study (Gunnars et al., 2004). Mg concentrations in deposits of

the HSM and BCL range between 0.2 and 1.56 wt. % (Sageman et al., 1997; Sageman et al., 1998) thus indicating that no precipitation of CFA in the water column should have occurred during either interval.

One potential mechanism for the disparity between the HSM and BCL in both the calculations of this study and geochemical data presented in Chapter 3 is the significant change in sedimentation rate across the boundary between these intervals. Sedimentation rates for the HSM (2.4 cm/kyr) are derived from the timescale of Gradstein et al. (2004) and are assumed constant throughout the interval. Previously published sedimentation rates for the BCL interval are based upon the development of an orbital timescale for OAE2 (Meyers et al., 2001; Sageman et al., 2006) and range between 1.02 – 0.42 cm/kyr with the greater values occurring in the lower BCL and lesser values in the upper BCL. These rates are consistent with observations indicating a major sea-level transgression across the boundary between these two units and maximum sea-level highstand occurring during the upper BCL interval (Arthur and Sageman, 2005; Laurin et al., 2005; Laurin and Sageman, 2001).

The observations of increased burial efficiency of P corresponding to increased sedimentation rates based upon geochemical (Chapter 3) and this modeling study agrees with previously published results that have made similar observations, particularly in deposits of the HSM. Ingall and Van Cappellen (1990) observed decreased $(C/P)_{org}$ values, despite redox conditions, at sedimentation rates greater than 1 cm/kyr. They attributed these observations to an increased burial efficiency of organic matter (OM) in such environments. The HSM is characterized by elevated OM

concentrations relative to the BCL and thus OM in this interval may have been buried at a rate sufficient to escape early diagenesis. Thus, the reactions necessary to release P from OM during early degradation processes would have been limited resulting in a mechanism for the decreased k_{rp} calculated in this study.

The trends observed by Ingall and Van Cappellen (1990) are not as apparent in deposits of the BCL however. Sedimentation rates in this interval vary between 0.4 and 1 cm/kyr. At such rates, one would expect enhanced burial of C_{org} relative to P and thus elevated C/P ratios (Ingall and Van Cappellen, 1990). However, geochemical and modeling results indicate extremely low burial efficiency of both organic C (C_{org}) (Meyers et al., 2005) and P (see Chapter 3) in this interval. Therefore, there must have been another mechanism controlling P burial besides sedimentation rate during deposition of the BCL.

One potential factor that can have a profound effect on P burial is the redox state of bottom and pore waters. Under oxygenated conditions, P released during OM degradation will preferentially sorb to available iron oxides and oxyhydroxides (Slomp et al., 1996a; Slomp et al., 1998). Such sorption prevents this P from being re-released back to the water column and eventually results in its precipitation as a P_{auth} mineral such as CFA. Two potential mechanisms can affect the efficiency of such sorption processes. First, the redox state of the water column will determine whether the iron oxides and oxyhydroxides are in an oxidized or reduced state. Secondly, there must be iron available in the water column regardless of redox conditions.

Proxy evidence, including molybdenum (Mo) accumulation (Meyers et al., 2005) and ichnofacies (Savirna, 1998), suggest that the lower BCL accumulated under oxygenated bottom and pore waters. Throughout the interval, pore and bottom waters became increasingly oxygen deficient with the most anoxic conditions occurring in the interval following OAE 2. Therefore, assuming an ample supply of oxides and oxyhydroxides, one would predict a low k_{rp} and enhanced P burial during the lower BCL with increasing k_{rp} and decreased P burial throughout the BCL. However, k_{rp} actually significantly increases at the HSM – BCL boundary and demonstrates an overall increase throughout the section (Fig. 4.2). Thus, the availability of iron oxides and oxyhydroxides in the water column may have been the primary factor controlling P regeneration during the BCL.

Based upon previously published bulk elemental data (Sageman and Lyons, 2003; Sageman et al., 1997; Sageman et al., 1998), Fe concentrations decrease from an average value in the HSM of 1.7 wt. % to an average value in the BCL of 1.1 wt. %. A potential flaw with utilizing bulk Fe concentrations is such measurements do not provide an accurate measurement of Fe-oxides that would have been available to sorb P released to the water column. A study in modern outer continental shelf sediments in the North Sea observed molar ratios of poorly crystalline Fe : P ranging from 9 – 14 depending on the extractant being used (~9 – 11 for NH_4 -oxalate; ~12 – 14 for oxalic acid) (Slomp et al., 1996b). A new extraction procedure for iron species (Poulton and Canfield, 2005) provides an opportunity to identify Fe-bearing phases into those that would have been highly reactive, and thus available to sorb P, versus those that would have been less reactive and unable to sorb P. Calculations of the molar ratios between

highly reactive Fe and P_{react} concentrations in ancient marine deposits may thus allow comparison to the observed trends between Fe and P concentrations in modern sediments (Slomp et al., 1996b). Such data is currently being collected by other authors from deposits of the USGS #1 Portland Core and ODP Site 1258 but is not yet available for this study interval.

4.5 IMPLICATIONS

Calculations of a significant increase in k_{rp} in deposits from the BCL relative to the HSM along with a short residence time of water in the basin could indicate that the KWIS was a major source of P to the global ocean during OAE 2. Such a scenario could be a significant breakthrough regarding our current understanding of the supply of nutrients to marine surface waters necessary to fuel the increased rates of primary production interpreted to be associated with this event (Kuypers et al., 2002). Current theories suggest that increased nutrient cycling in an oxygen deficient ocean maintained the supply of P to the photic zone in a manner similar to the productivity – anoxia feedback (PAF) mechanism originally put forth by Ingall et al. (1993) (Mort et al., 2007; Nederbragt et al., 2004). In chapter 3 of this dissertation I suggest that the global ocean may have been preconditioned to a state favorable to support the PAF model by increased P delivery via riverine sources associated with increased chemical weathering preceding the event. However, calculations here combined with the observations of decreased P burial during deposition of the BCL despite increased productivity rates indicate that shallow epicontinental seas such as the KWIS may have provided an additional source of P to the global ocean during OAE 2 in a manner not previously considered.

4.6 CONCLUSIONS

Preliminary modeling results of the biogeochemical cycling of P in the KWIS during the C – T OAE 2 interval indicate enhanced burial of P during deposition of the HSM and greater regeneration of P reaching the sediments via OM during deposition of the BCL. The increased burial of P during the HSM appears to be directly related to increased sedimentation rates during this interval (Gradstein et al., 2004; Ingall and Van Cappellen, 1990). Decreased P burial during the BCL seems to be more difficult to explain. Sedimentation rates (Meyers et al., 2001; Sageman et al., 2006) and oxygenation of bottom and pore waters (Meyers et al., 2005; Savrda, 1998) during this interval provide proxy evidence that would suggest conditions favorable for enhanced P burial during this interval. One potential explanation of such contrasting evidence could be a decreased supply of Fe-oxides available to sorb P released during oxic degradation of OM. However, further work is needed to test this hypothesis. Such conditions of decreased P burial during the BCL does indicate that shallow epicontinental seas such as the KWIS may have been a significant source of this biolimiting nutrient to the global ocean during this interval of increased rates of primary production in the global ocean.

CHAPTER 5

UTILIZATION OF THE SEDEX METHOD TO DETERMINE THE SOURCES OF PHOSPHOROUS TO MARINE SURFACE WATERS DURING THE FRASNIAN – FAMENNIAN MASS EXTINCTION EVENT

5.1 INTRODUCTION

One of the many environmental concerns to result from anthropogenic activities over the last 150 years has been the potential for eutrophication of modern rivers, lakes, and shallow marine environments due to increases in nutrient-rich runoff. Eutrophication results mainly from changes in land use activities associated with agriculture and deforestation (Turner et al., 2003). It has been shown that oxygen-deficient conditions in several shallow marine systems of the United States coastal realm are directly caused by eutrophication due to increased nutrient supply from anthropogenic fertilization of agricultural lands (Cole et al., 2004; Rabalais and Turner, 2006). However, the net result, if this process continues, is poorly understood. One interval of the geologic past that may provide insight into future responses of shallow marine environments undergoing eutrophication is the Frasnian – Famennian (F – F) biotic crisis.

The F – F boundary interval has been classified as one of the five major mass extinction events of the Phanerozoic (Sepkoski, 1986). Although culminating at the F – F boundary itself, the extinction spanned as much as 3 myr (McGhee, 1996). The ecological extent of the extinction was greatest among low-latitude, shallow water reef building organisms (Joachimski and Buggisch, 1993; Stearn, 1987; Thompson and

Newton, 1988). Based on analysis of observational data across a wide range of environments, the main causal mechanisms that have been proposed include bolide impacts (McGhee, 2001; Wang et al., 1991; Yan et al., 1993), climate change (Copper, 1986; Joachimski and Buggisch, 2002; McGhee et al., 1986; Ormiston and Oglesby, 1995) and ocean anoxia (Algeo et al., 1995; Algeo and Scheckler, 1998; Joachimski and Buggisch, 1993; Joachimski et al., 2001; Murphy et al., 2000a; Wang et al., 1996).

Coincident with the extinction interval are two periods of enhanced organic carbon (C_{org}) accumulation known as the Lower and Upper Kellwasser horizons. Each of these intervals corresponds to a globally correlative positive $\delta^{13}C$ excursion (Bond et al., 2004; Buggisch and Joachimski, 2006; Joachimski and Buggisch, 1993; Joachimski et al., 2002; Sageman et al., 2003). Typically these intervals have been interpreted to reflect deposition under dysoxic to anoxic conditions, although recent studies suggest some variations in the extent and degree of such conditions (Bond et al., 2004). The overall widespread occurrence of such deposits during the extinction interval lends credence to the hypothesis that ocean anoxia at least played some role in the extinction event.

Much debate in recent literature has centered on the exact cause of anoxia associated with the Lower and Upper Kellwasser events. It is assumed that increased rates of primary production were associated with the development of dysoxic – anoxic facies observed in these intervals (Algeo et al., 1995; Algeo and Scheckler, 1998; Murphy et al., 2000a; Sageman et al., 2003). However, the source of nutrients necessary to initiate and maintain this hypothesized productivity has remained poorly

constrained. One leading hypothesis suggests that increased chemical weathering rates due to the evolution and spread of vascular plants led to increased fluxes of terrestrially derived nutrients to the marine realm (Algeo et al., 1995; Algeo and Scheckler, 1998). A more recent study has suggested that an additional, and perhaps more significant, supply of terrestrially derived nutrients may have been sourced from uplifted terrains associated with orogenic events that occurred across several continents during this period (Averbuch et al., 2005; Tribovillard et al., 2004). An alternative mechanism known as the “productivity – anoxia feedback” (PAF) model (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Ingall et al., 1993; VanCappellen and Ingall, 1994) was also proposed to explain both increased rates of primary production and continued anoxia in the Lower and Upper Kellwasser horizons, as well as other black shales of the Devonian Appalachian Basin (DAB) (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003). In their study of the F – F black shales, Murphy et al. (2000a) observed consistent changes in multi-proxy geochemical data, including $(C/P)_{org}$ ratios, that suggested extensive loss of phosphorus (P) during organic matter (OM) decomposition under fluctuating redox conditions.

This study utilized the SEDEX method (Anderson and Delaney, 2000; Ruttenberg, 1992) along with previously published C_{org} and trace element data (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003) in an effort to reconcile the alternate hypotheses discussed above. It is assumed that over geologic timescales P acts as the principal biolimiting nutrient to marine primary production (Bjerrum and Canfield, 2002; Tyrrell, 1999). Therefore, utilization of the SEDEX method to differentiate reactive P (P_{react}) minerals formed *in situ* versus detrital apatite (P_{det})

minerals transported from the terrestrial realm, along with comparisons to other detrital and redox proxies, may help to clarify the potential sources of nutrients that could have resulted in the increased primary production interpreted for the Lower and Upper Kellwasser events.

5.2 METHODS

Samples spanning the Lower and Upper Kellwasser horizons were obtained from the NX-1 West Valley drill core from western New York State (Fig. 2.3). The sampling interval ranged between 10 – 60 cm. Concentrations of C_{org} and trace elements from the same core depths were obtained from previously published results (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003). The SEDEX sequential extraction procedure (Anderson and Delaney, 2000; Ruttenberg, 1992) was applied to each sample to quantify the different P phases. See Chapter 1 and Figure 1.1 for a description of each phase and the extraction procedures utilized. Ratios of C_{org}/P_{react} are utilized to test the PAF hypothesis proposed by Murphy et al. (2000a) while P_{det} is utilized as a potential proxy for terrestrially derived nutrient inputs (see Chapter 2).

Comparison of P data collected here to other detrital and redox proxies for this interval will aid in interpretations of the relative roles of terrestrial input versus nutrient regeneration in the water column as the dominant process controlling putative increased rates of primary production associated with the Lower and Upper Kellwasser events. Redox proxies utilized in this study include V + Cr and Mo concentrations. Increases in V + Cr concentrations have been interpreted to represent dysoxic marine conditions under which the dominant OM degradation process is nitrogen fixation (Piper, 1994). Increases in Mo concentrations have been associated with anoxic to euxinic conditions and represent sulfate reduction as the predominant mechanism of OM degradation (Crusius et al., 1996; Emerson and Huested, 1991; Helz et al., 1996; Meyers et al., 2005). Changes in the ratios Ti/Al and Si /Al are utilized to reflect changes in detrital

input. An increase in both ratios is interpreted to represent an increase in detrital deposition as it suggests an increase in the proportion of coarser grain fractions relative to clays (Bertrand et al., 1996).

5.3 RESULTS

Both the Lower and Upper Kellwasser events are characterized by a 3 – 4 ‰ positive $\delta^{13}\text{C}_{\text{org}}$ excursion, deposition of C_{org} –rich (2 – 6 wt. %) laminated black shales (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003), and elevated $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ ratios between 300 - 600 (Figs 5.1 and 5.2). The details of each interval are discussed below.

5.3.1 Lower Kellwasser

The Lower Kellwasser interval studied in the NX-1 West Valley core spans the upper 4m of fine grained sandstone of the Nunda Formation, the laminated black shales of the 4 m thick Pipe Creek Shale, and the lowermost meter of silty, greenish gray mudstones of the Hanover Formation (Sageman et al., 2003). Concentrations of C_{org} in the laminated black shales range between 3 – 5 wt. % while values in the non-laminated mudstones are less than 1 wt. % (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003) (Fig. 5.1). Concentrations P_{react} are slightly lower in the laminated black shale facies of the Pipe Creek Shale with average values of 9.5 $\mu\text{mol/g}$ versus 11.23 $\mu\text{mol/g}$ in the uppermost Nunda and lowermost Hanover Formations (Figs 5.1 and 5.3). Values of $\text{C}_{\text{org}}/\text{P}_{\text{react}}$ in the C_{org} –rich deposits reach 300 - 600 while those in the intervals prior to and following the event are less than the Redfield ratio of ~ 100 (Redfield, 1958). Similar trends, although with significantly greater values, have been demonstrated for $(\text{C/P})_{\text{org}}$ in previous studies (Murphy et al., 2000a).

Redox proxies indicate that oxygen-deficient conditions prevailed during

Figure 5.1. Data for the Lower Kellwasser Horizon including the uppermost Nunda Formation, Pipe Creek Shale, and lowermost Hanover Formation. Includes $\delta^{13}\text{C}$, P phases, C_{org} , $C_{\text{org}}/P_{\text{react}}$, and proxies for redox conditions (V + Cr and Mo concentrations). All concentration data except the P phases from Sageman et al. (2003). Dashed lines represent background average values (Sageman et al., 2003).

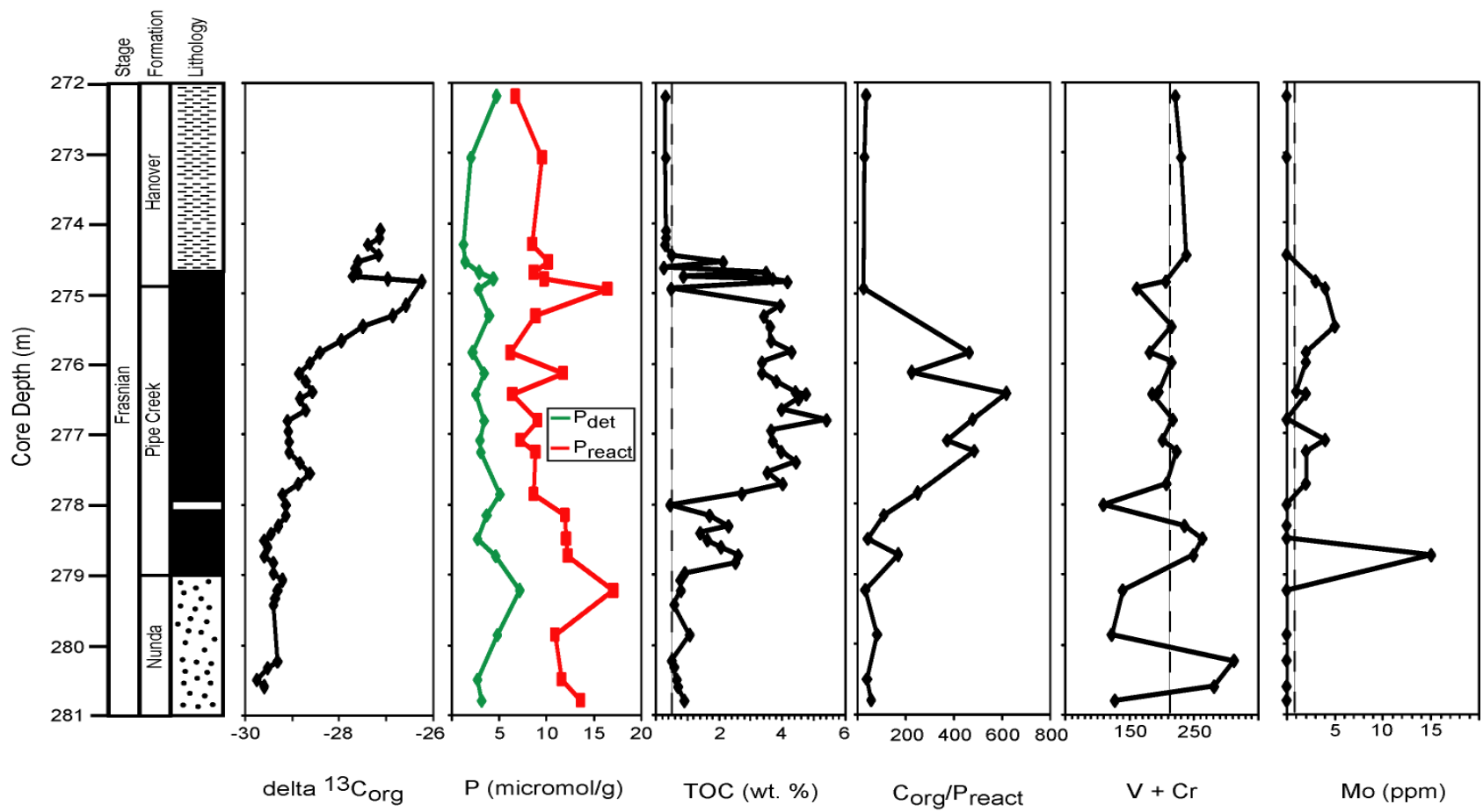


Figure 5.1

Figure 5.2. Data for the Upper Kellwasser horizon spanning the uppermost Hanover Formation including the F – F boundary. Includes $\delta^{13}\text{C}$, P phases, C_{org} , $\text{C}_{\text{org}}/\text{P}_{\text{react}}$, and proxies for redox conditions (V + Cr and Mo concentrations). All concentration data except the P phases from Sageman et al. (2003). Dashed lines represent background average values (Sageman et al., 2003).

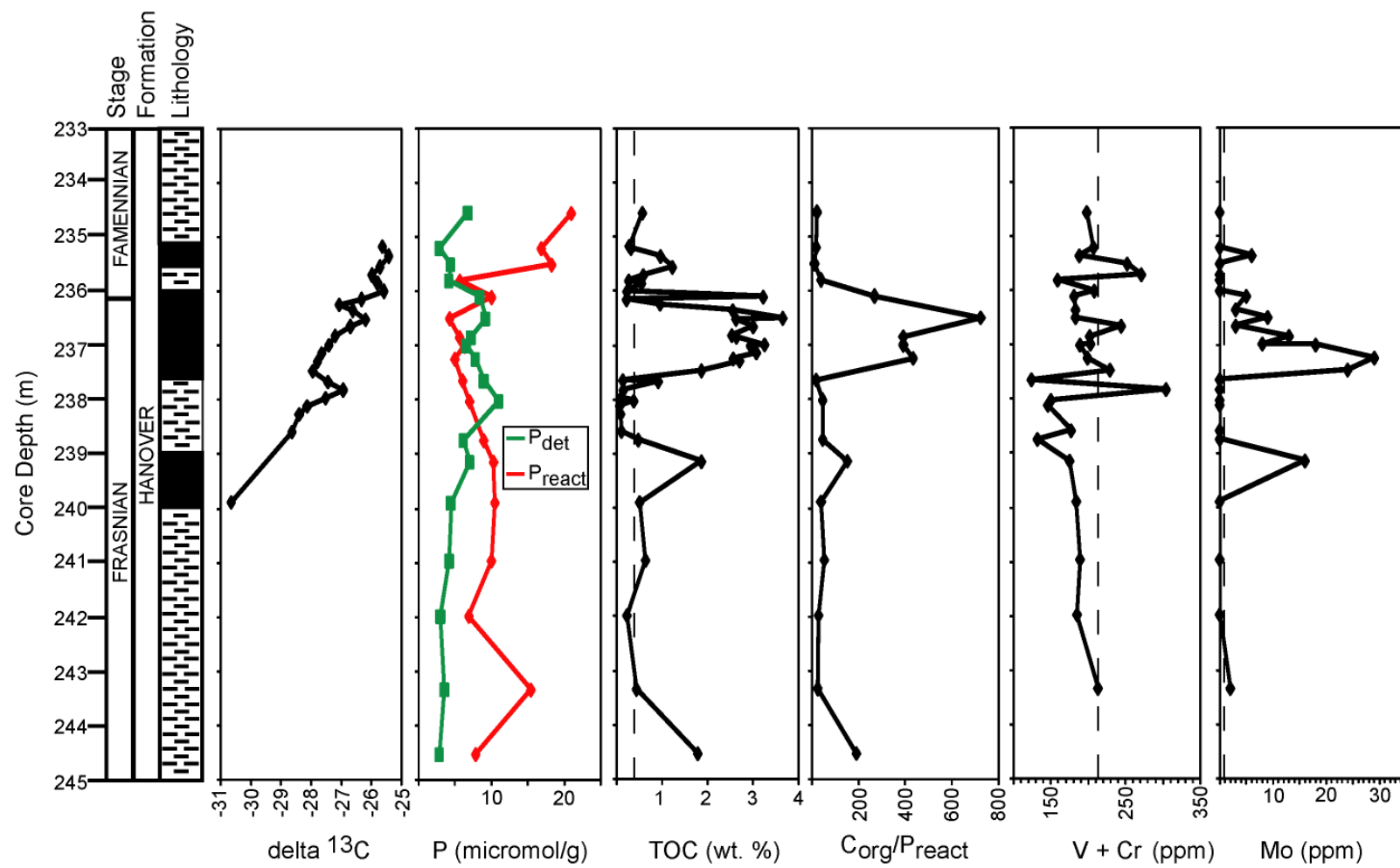


Figure 5.2

Figure 5.3. Data for the Lower Kellwasser Horizon including the uppermost Nunda Formation, Pipe Creek Shale, and lowermost Hanover Formation. Includes $\delta^{13}\text{C}_{\text{org}}$, concentration of P phases, $\text{P}_{\text{tot}}/\text{Al}$, and the detrital proxies Ti/Al and Si/Al . Concentration data for the elemental ratios (except for P_{tot}) as well as $\delta^{13}\text{C}_{\text{org}}$ were obtained from Sageman et al. (2003). Dashed lines represent average background values (Sageman et al., 2003).

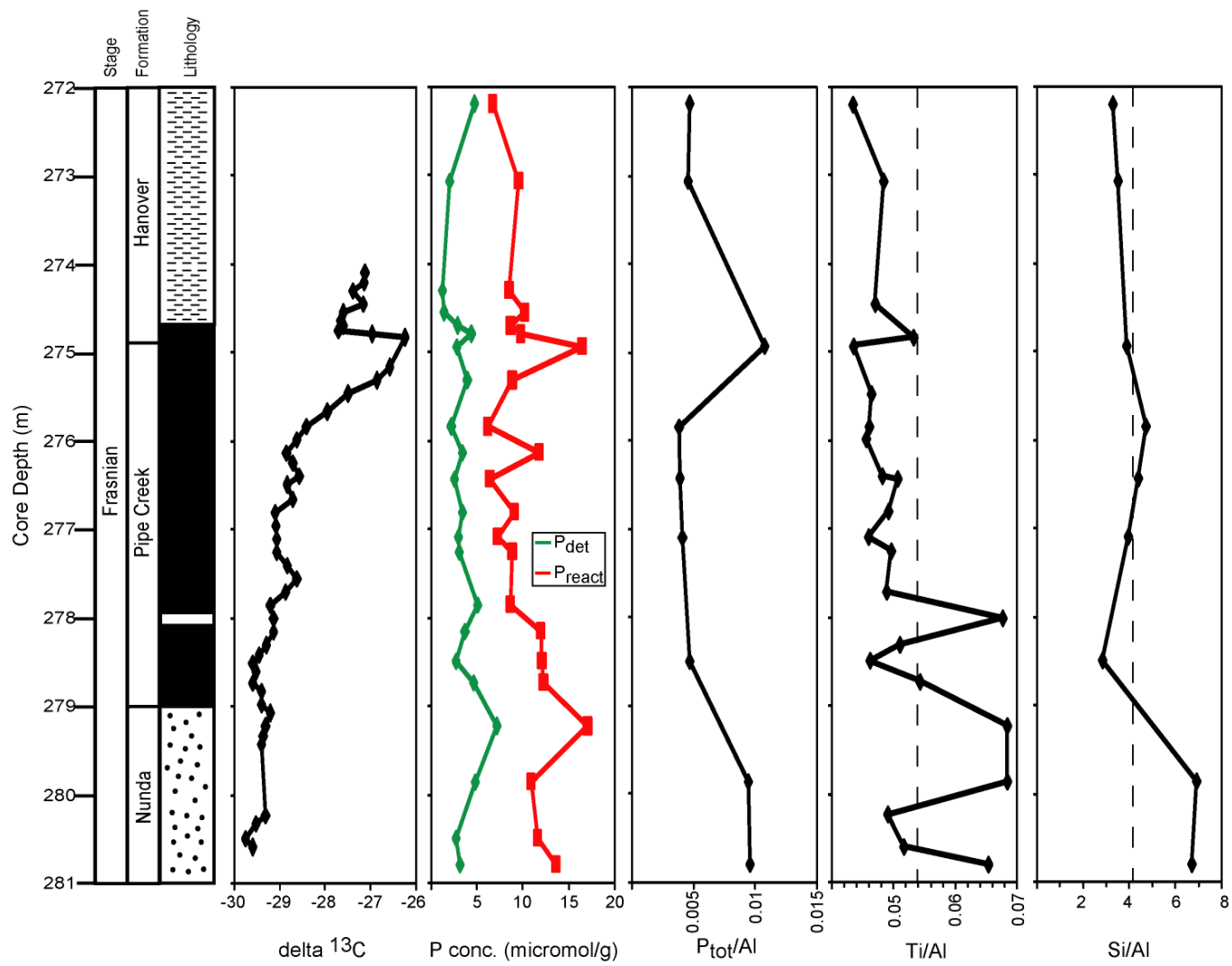


Figure 5.3

deposition of the C_{org} –rich black shales of the Lower Kellwasser event. However, the degree of oxygen deficiency varies. Values of $V + Cr$ does not vary above 1 standard deviation of the background average value (defined as the average value of all measured values of the Genesee Formation by Sageman et al. (2003)) throughout the Pipe Creek Shale and Mo concentrations show enriched values only at the onset and end of the interval of peak C_{org} accumulation (Sageman et al., 2003) (Fig. 5.1). Thus, it appears that oxygen deficiency did occur but euxinia was restricted to the interval of time characterized by maximum C_{org} burial.

Detrital proxies in the Lower Kellwasser also show little variation following deposition of the Nunda Formation. In the uppermost Nunda, both Ti/Al and Si/Al are elevated above 1 standard deviation relative to background average values which would be expected in a fine-grained quartz sandstone facies. Above the Nunda, Ti/Al and Si/Al are generally at or below background average values through the lowermost Hanover Formation, consistent with deposition of a condensed black shale (Sageman et al., 2003) (Fig. 5.3). Concentrations of P_{det} show a similar trend with average concentrations in the Nunda Formation of 4.44 $\mu\text{mol/g}$ and average values in the Pipe Creek Shale and lowermost Hanover Formation of 3.15 $\mu\text{mol/g}$.

5.3.2 Upper Kellwasser

The Upper Kellwasser Horizon spans the lithologic transitions between silty greenish-grey mudstones and laminated black shale facies of the uppermost 12 m of the Hannover Formation. Concentrations of C_{org} range between near-zero in the mudstones to between 2 – 4 wt. % in the C_{org} –rich black shales (Sageman et al., 2003)

(Fig. 5.2). P_{react} concentrations are significantly reduced in the black shale facies with average values of $6.19 \mu\text{mol/g}$ versus an average value of $11.1 \mu\text{mol/g}$ in the greenish-grey mudstone facies. Values of $C_{\text{org}}/P_{\text{react}}$ range between 400 – 800 in the C_{org} –rich black shales but are generally less than 100 in the mudstone facies before and after the event (Fig. 5.2). A similar trend has also been observed for $(C/P)_{\text{org}}$ values from the same samples in a previous study (Murphy et al., 2000a).

Redox proxies indicate oxygen-deficient conditions coincident with deposition of C_{org} –rich laminated black shales. Both V + Cr and Mo concentrations increase at the onset of enhanced C_{org} concentrations (Fig 5.2). Mo concentrations then steadily decline until reaching zero at the end of the interval of black shale deposition. Concentrations of V + Cr peak following maximum C_{org} deposition and remain elevated relative to the interval prior to black shale deposition throughout the rest of the Hanover Formation (Fig. 5.2) thus indicating the prevalence of relative oxygen deficiency during and following the Upper Kellwasser event.

Detrital proxies (Fig. 5.4) all indicate increased terrestrial input prior to the onset of black shale deposition followed by a decline consistent with development of a condensed black shale during a sea-level rise event. This trend is consistent for Ti/Al, Si/Al, and $P_{\text{det.}}$ (Fig. 5.4).

Figure 5.4. Data for the Upper Kellwasser horizon spanning the uppermost Hanover Formation including the F – F boundary. Includes $\delta^{13}\text{C}$, P phases, P_{tot}/Al , and the detrital proxies Ti/Al and Si/Al . Concentration data for the elemental ratios (except for P_{tot}) as well as $\delta^{13}\text{C}_{\text{org}}$ were obtained from Sageman et al. (2003). Dashed lines represent average background values (Sageman et al., 2003).

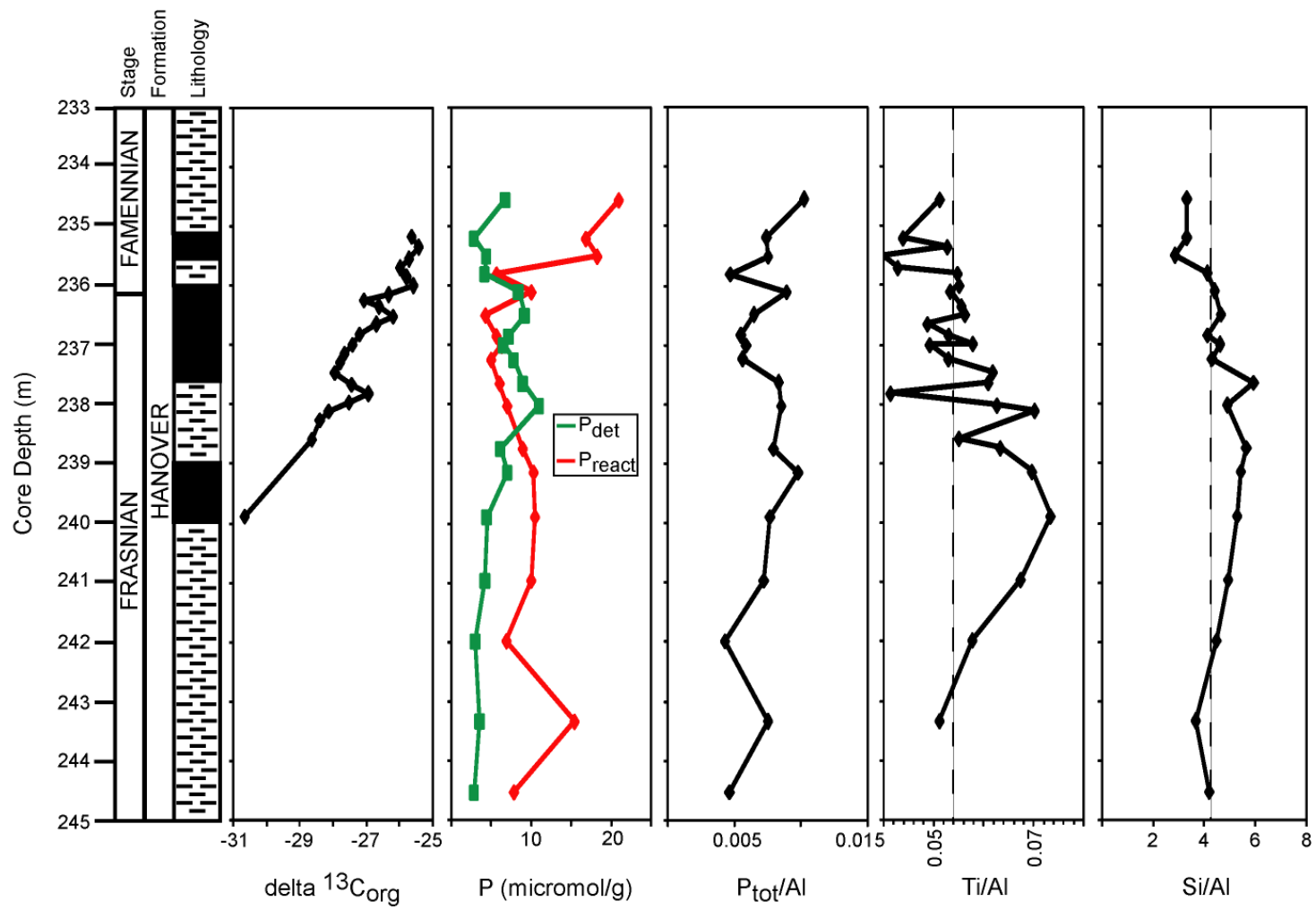


Figure 5.4

5.4 DISCUSSION

Two alternate hypotheses have been proposed to explain increased rates of marine primary production interpreted to be associated with deposition of C_{org} -rich laminated black shales of the Lower and Upper Kellwasser horizons. The first states that increased rates of chemical weathering resulted in higher fluxes of terrestrially derived nutrients to marine surface waters (Algeo et al., 1995; Algeo and Scheckler, 1998; Averbuch et al., 2005; Tribovillard et al., 2004). The second hypothesis suggests that the PAF mechanism (Ingall and Jahnke, 1994; Ingall and Jahnke, 1997; Ingall et al., 1993; VanCappellen and Ingall, 1994) is an important source of enhanced nutrient levels during each event (Murphy et al., 2000a).

In this study, I utilized the SEDEX method to address these alternate hypotheses. The SEDEX method can accomplish this by separating the operationally defined phases of measured P into P_{react} and non-reactive species (Fig. 1.1). By definition, P_{react} species consist of those phases believed to represent the bioavailable P reservoir in the water column (Anderson et al., 2001). The only non-reactive phase is P_{det} , which derives from igneous and metamorphic apatite minerals transported to marine sediments via riverine or eolian processes, and thus potentially serves as a proxy for terrestrially derived bioavailable P to the marine realm (since it reflects the relative amount of P liberated by weathering; see Chapter 2). The remainder of this section will address each alternate hypothesis for the Lower and Upper Kellwasser horizons independently, and then present a conceptual model that takes into account observations from both horizons.

5.4.1 Lower Kellwasser

The Lower Kellwasser Horizon above the Nunda Formation is interpreted as having been deposited under variable degrees of oxygen deficiency (Sageman et al., 2003). Anoxic conditions were most prevalent (based on increased Mo concentrations) during deposition of the laminated, C_{org} –rich black shales of the Pipe Creek Shale. These conditions coincide with a five to six fold increase in C_{org} concentrations, a 15 % decrease in P_{react} concentrations, and greater than an order of magnitude increase in C_{org}/P_{react} values (Fig. 5.1). Such evidence is consistent with the PAF mechanism as a cause of increased concentrations of C_{org} .

Detrital proxy data, including P_{det} concentrations, Ti/Al, and Si/Al are all elevated in deposits of the uppermost Nunda Formation. Above the Nunda, all detrital proxies initially decrease and then remain relatively constant throughout the remainder of the Lower Kellwasser horizon. Thus, it is possible that an increased detrital flux during deposition of the uppermost Nunda Formation preceded the onset of deposition of C_{org} –rich black shale facies characteristic of the Pipe Creek Shale and provided the necessary nutrients to precondition the DAB to a eutrophic state.

The shift in facies from a fine-grained quartz sand of the Nunda Formation to the laminated black shales of the Pipe Creek Shale is also indicative of a sea-level rise event at this time. Sea-level rise events have been correlated to black shale deposition throughout this interval (Johnson and Sandberg, 1988; Sageman et al., 2003). Such a sea-level rise may have served as a catalyst for OM burial via sediment starvation (Sageman et al., 2003) and potential release of nutrients from shallow marine

sediments. This scenario is similar to one recently suggested by Filippelli et al. (2007) to explain increased rates of primary production interpreted to occur at the end of the Pleistocene glaciations. The reduction of terrestrial input combined with a decrease in P_{tot}/A_I (indicating significantly reduced burial of P_{det} and P_{react}) (Fig. 5.3) provides further evidence for a rise in sea-level and subsequent initiation of a PAF mechanism resulting in favorable conditions for maintaining enhanced C_{org} burial and preservation (Demailson and Moore, 1980) throughout the Lower Kellwasser event.

5.4.2 Upper Kellwasser

The Upper Kellwasser horizon spans the F-F boundary and represents the culmination of the Late Devonian mass extinction event (McGhee, 1996; Sepkoski, 1986). The laminated black shales of the upper Hanover Formation can be correlated to similar lithologies deposited in shallow marine environments globally at this time (Bond et al., 2004; Buggisch and Joachimski, 2006; Chen et al., 2002; Joachimski and Buggisch, 1993; Joachimski et al., 2001; Joachimski et al., 2002; Murphy et al., 2000a; Murphy et al., 2000b; Over, 2002; Sageman et al., 2003). Geochemical studies of these facies have indicated water column anoxia and possible photic zone euxinia that were interpreted to result from increased rates of primary production (Chen et al., 2005; Joachimski et al., 2001; Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003). Although Murphy et al. (2000a) suggested that the PAF mechanism sourced nutrients to marine surface waters and thus increased rates of productivity during the Upper Kellwasser; it has remained unclear whether this was the only source of nutrients to the basin.

Evidence from this study may provide support for both of the alternate hypotheses that have been suggested in prior studies (Algeo et al., 1995; Algeo and Scheckler, 1998; Averbuch et al., 2005; Murphy et al., 2000a; Tribovillard et al., 2004). Enhanced terrestrial input, reflected in greater concentrations of P_{det} and other detrital proxies, does appear to occur prior to the deposition of laminated C_{org} –rich black shales (Fig. 5.4). This flux of terrestrial material may have acted to precondition shallow marine environments towards a state of eutrophication. An increase in P_{tot}/Al following the onset of increased detrital input (Fig. 5.4), but prior to the onset of marine anoxia, provides further evidence that the enhanced terrigenous input was supplying bioavailable P and causing increased rates of primary production as increases in P_{tot}/Al have been used as a proxy for elevated export production in Eocene to Miocene deposits in the Southern Ocean (Latimer and Filippelli, 2002). It is therefore suggested that this preconditioned ocean began the process of eutrophication and oxygen consumption throughout the water column.

Similar to observations in the Lower Kellwasser horizon, the onset of deposition of the C_{org} –rich facies of the Upper Kellwasser have been linked to a sea-level rise event (Chen et al., 2002; Johnson et al., 1985; Johnson and Sandberg, 1988). Thus, a similar mechanism may be applied to explain the development of conditions necessary to initiate a PAF mechanism during the Upper Kellwasser event as well. This scenario agrees with previous interpretations of sea-level rise events creating the necessary conditions for enhanced productivity and coincident burial and preservation of C_{org} –rich facies via clastic starvation, seasonal to longer term stratification of the water column,

and release of nutrients from shallow marine sediments (Filippelli et al., 2007; Godderis and Joachimski, 2004; Sageman et al., 2003).

5.4.3 Conceptual Model

A conceptual model incorporating each of the perturbations in nutrient fluxes hypothesized to have controlled deposition of C_{org} –rich facies in the DAB is described here. The initial conditions of this model represent an average background rate of terrestrial input and primary production. Under such conditions, the basin remains oxic and terrestrial nutrient supply is relatively low, limiting C_{org} and P_{react} burial in shallow marine sediments. The initial perturbation to the system is an increase in the terrestrial flux, including P_{det} . This results in slight increases in both C_{org} and P_{react} burial (Figs. 5.1 and 5.3), as well as P_{tot}/Al (Fig 5.4). It is thus assumed that the increase in primary production is associated with an increased terrestrial nutrient supply (Fig. 5.4).

Enhanced primary production along with a sea-level rise eventually results in siliciclastic sediment starvation and oxygen-deficient conditions in marine bottom and pore waters. This is indicated by increases in both $V + Cr$ and Mo concentrations (Meyers et al., 2005; Piper, 1994) (Figs. 5.1 and 5.3). During this interval, Ti/Al and Si/Al return to background values. However, P_{det} remains elevated in the Upper Kellwasser event suggesting that a continued supply of terrestrially derived nutrients may

have provided additional nutrients to those released in a PAF type mechanism during deposition of the C_{org} -rich black shale facies. However, an order of magnitude increase in the C_{org}/P_{react} ratios in these facies suggests that the PAF mechanism was the primary source for nutrient supply to marine surface waters. The series of events described above demonstrate that a conceptual model, taking into account enhanced terrestrial input, relative sea-level rise, and the productivity – anoxia feedback mechanism, may best explain observations from the Lower and Upper Kellwasser horizons in the DAB.

5.5 CONCLUSIONS

Results from this study suggest that an increased terrestrial flux of biolimiting dissolved reactive P was delivered to marine surface waters preceding the onset of marine anoxia and deposition of C_{org}-rich laminated black shale facies characteristic of the Upper and Lower Kellwasser events. This increased flux of terrestrially derived P caused increased rates in marine primary production and subsequent consumption of oxygen throughout the water column due to OM degradation. These factors, coupled with subsequent sea-level rise and sediment starvation, led to an oxygen-deficient water column and conditions favorable for the development of a PAF type mechanism. PAF-generated nutrients sustained increased rates of primary production under conditions favorable for the burial and preservation of OM and hence the deposition of the C_{org}-rich laminated black shale facies of the Lower and Upper Kellwasser horizons.

CHAPTER 6

THE ATMOSPHERIC SUPPLY OF TERRESTRIAL AUTHIGENIC PHOSPHATE MINERALS TO MARINE SEDIMENTS

6.1 INTRODUCTION

In recent years, efforts have increased to reconstruct the marine paleo-phosphorus (P) cycle owing to the impact of P availability on biological processes that regulate seawater and sedimentary geochemistry and possibly, periods of climate change throughout Earth history (Bjerrum and Canfield, 2002; Filippelli et al., 2007). Development and widespread implementation of sequential extraction procedures for analyzing patterns of P enrichment and occurrence in marine sediments have been especially vital to such efforts. Chief among these, the SEDEX method (Anderson and Delaney, 2000; Ruttenberg, 1992) enables quantification of operationally defined P-bearing species that relate to the primary reactive P pool in diverse depositional environments. These species include P adsorbed to oxides and oxyhydroxides (P_{ox}), authigenic apatite minerals (P_{auth}) such as carbonate fluorapatite (CFA), detrital apatite minerals (P_{det}), such as hydroxyapatite and fluorapatite, and P within remnant organic matter (P_{org}). These phases are considered either reactive (P_{react}) or non-reactive, with P_{react} equaling the sum of P_{ox} , P_{auth} , plus P_{org} (Anderson et al., 2001). The reactive phases are assumed to represent the net burial of dissolved P that was originally bioavailable in the depositional environment. Only P_{det} is considered non-reactive.

Because changes in the burial efficiency of P_{react} directly influence P availability, trends in sedimentary P analyzed using SEDEX can be effectively related to changes in

productivity and/or redox conditions. In this way, SEDEX has profoundly influenced views of P cycling (Compton et al., 2000; Delaney, 1998; Filippelli, 2002; Ruttenberg, 2003; Ruttenberg and Berner, 1993). For example, research showing that P_{auth} represents the ultimate sink of P released during early diagenesis and associated organic matter (OM) degradation has led to a downward revision of the residence time of P in the modern ocean from ~80 kyr (Froelich et al., 1982) to 10 - 17 kyr (Ruttenberg, 2003). Application of SEDEX has also affected interpretations of molar C_{org}/P ratios (Anderson et al., 2001). Whereas initial studies used variations in $(C/P)_{\text{org}}$ ratios as a proxy for redox and productivity conditions in the geologic past (Ingall et al., 1993; Murphy et al., 2000a; Nederbragt et al., 2004), recent work has demonstrated that $C_{\text{org}}/P_{\text{react}}$ ratios provide a more reliable proxy because the operationally defined P_{react} pool offers the best estimate of P released during OM degradation (Anderson et al., 2001).

However, a fundamental assumption underlying these and other interpretive links is that P_{auth} forms entirely *in situ* during redox-controlled precipitation of CFA. To our knowledge, few studies have quantified the speciation of P in source sediments or estimated the potential of P_{auth} contributions from terrestrial sources. In their seminal study employing SEDEX, Ruttenberg and Berner (1993) identified three additional P-bearing phases that may be assayed by the step designed to quantify P_{auth} . These phases include P within fish debris, P within carbonate minerals, and P within smectite. Studies have reported these phases in sediments of the North Atlantic and North Sea (Slomp et al., 1996a) and the Gulf of St. Lawrence (Louchouart et al., 1997). Because P within fish debris and carbonate minerals most likely originates as P_{react} , its inclusion

in P_{auth} estimates does not introduce errors to P_{react} summations but will compromise abilities to isolate *in situ* P_{auth} formation. In contrast, smectite has a detrital source, and lattice-bound P may not be associated with the marine P cycle; the P within such minerals may be misrepresented as P_{react} (Louchouart et al., 1997). This study tests whether dust deposition influences P_{auth} accumulation in modern marine sediments in the North Pacific Ocean (NPO) and Japan Sea (Fig 6.1) by using SEDEX to quantify the speciation of P in loess from the Chinese Loess Plateau, the predominant source of dust to these ocean basins.

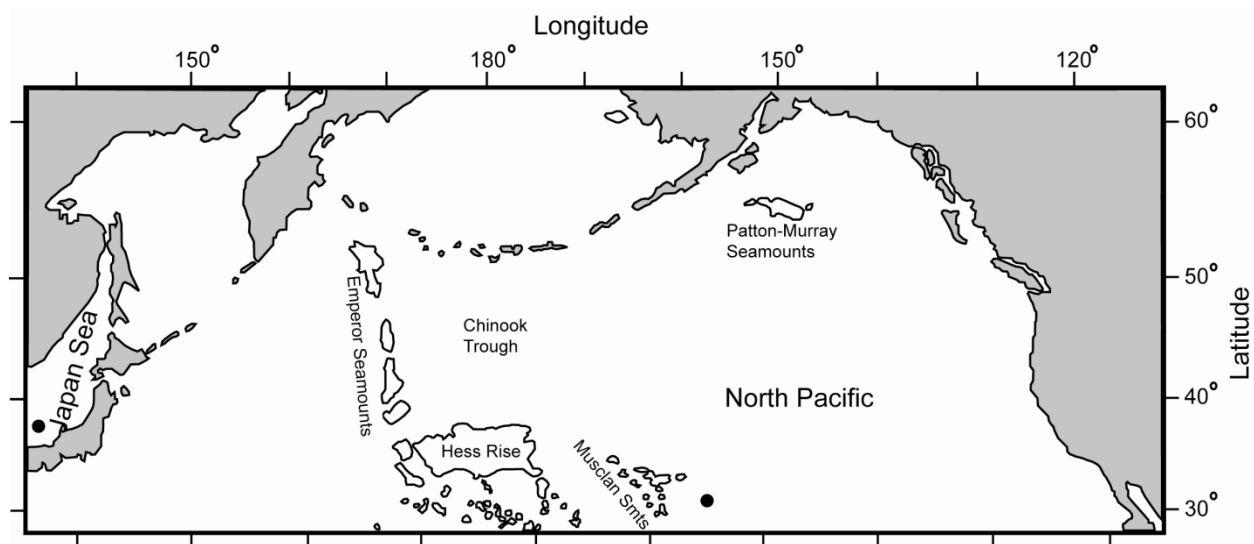


Figure 6.1. Map of North Pacific Ocean with filled circles showing the location of core LL44-GC3 and the approximate location of sites in the Japan Sea studied by Cha et al. (2005). Adapted from Rea et al. (1998).

6.2 METHODS

SEDEX was applied to the $<2\ \mu\text{m}$ fraction of ten loess samples collected from locations throughout the Chinese Loess Plateau. The samples are age correlative with the last glacial maximum through the Holocene and include typical loess horizons and weakly developed soils. As demonstrated by Jacobson (2004) and Jacobson and Holmden (2006), the samples are geochemically and mineralogically identical to Chinese Loess and desert sands from other locations and time periods. We measured P concentrations using a Shimadzu UV-1601 UV-visible spectrophotometer. Color development for each extractant was achieved utilizing standard molybdate blue methodologies (Strickland and Parsons, 1972). Relative errors for each SEDEX step are 10.2% (P_{ox}), 1.1% (P_{auth}), 3.5% (P_{det}), and 9.8% (P_{org}).

6.3 RESULTS

Appendix _ reports raw concentration measurements and Figure 2 displays the occurrence of P within the samples. Bulk loess contains total P concentrations (P_{tot}) between 12.11 and 18.52 $\mu\text{mol/g}$ with an average of 15.25 $\mu\text{mol/g}$. Most P occurs as P_{auth} (28.39 – 54.35%; avg. = 41.93%) and P_{det} (26.64 – 61.87%; avg. = 42.49%) followed by P_{ox} (8.14 – 25.37%; avg. = 13.53%) and P_{org} (0.81 – 2.95%; avg. = 2.06%). Relative to bulk loess, P occurs as P_{auth} (4.22-10.06 P_{auth} $\mu\text{mol/g}$, avg. = 6.47 $\mu\text{mol/g}$); P_{det} ((2.86 – 9.95 $\mu\text{mol/g}$, avg. = 6.49 $\mu\text{mol/g}$); P_{ox} (1.31 – 2.76 $\mu\text{mol/g}$, avg. = 1.99 $\mu\text{mol/g}$); and P_{org} (0.13 – 0.47 $\mu\text{mol/g}$, avg. = 0.30 $\mu\text{mol/g}$). The bulk P concentrations reported here agree well with values reported for other studies of Chinese Loess. For example, Gallet et al. (1996) reported P_{tot} concentrations between 16.92 and 23.94 $\mu\text{mol/g}$ for dust and desert sands collected from the Louchuan section. To our knowledge, no studies have apportioned P among different phases in samples taken directly from the Chinese Loess Plateau. Using a revised SEDEX methodology (Berner and Rao, 1994), Chen et al. (2006) analyzed the distribution of P within particulate aerosols collected over Taiwan and found comparable concentrations of P_{tot} but more P_{det} and less P_{auth} relative to this study. The latter differences likely reflect subtle mineralogical variations in provenance, as no dust storms emanating from the Chinese Loess Plateau occurred when the aerosols were collected (Chen et al., 2006).

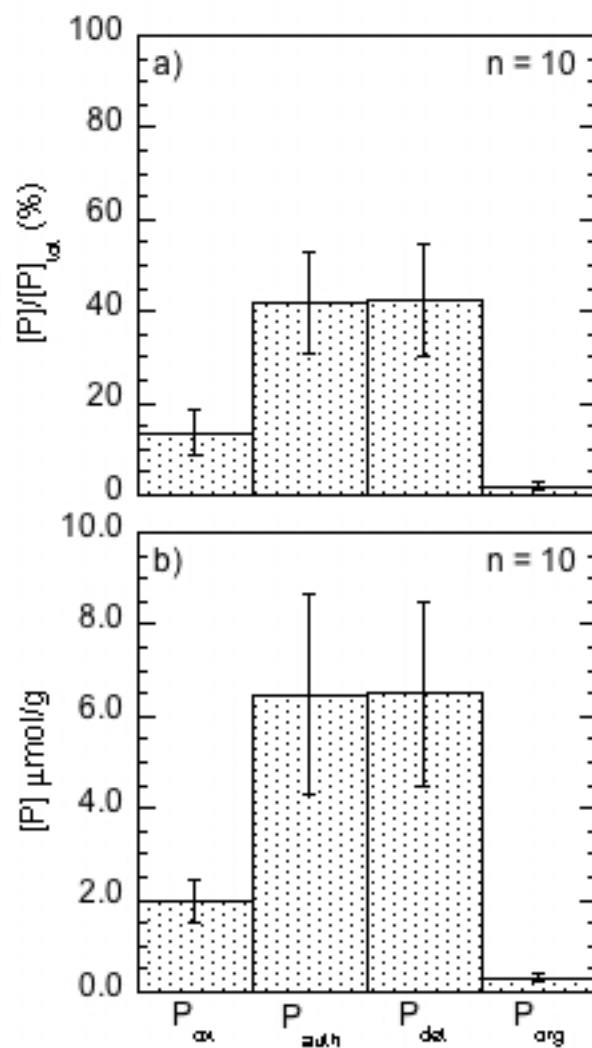


Figure 6.2. Bar graphs showing relative (a) and absolute (b) abundances of P-bearing phases in Chinese Loess. Error bars denote 1 σ uncertainty.

6.4 DISCUSSION

Arid regions in northern and eastern Asia, including the Chinese Loess Plateau, are the primary sources of dust supplied to the NPO and its marginal seas (Asahara et al., 1995; Duce et al., 1991; Nakai et al., 1993). These sources have remained stable throughout the Late Cenozoic (Pettke et al., 2000; Rea et al., 1998). Findings presented here underscore the importance of dust deposition for the accumulation of P in surface sediments from the central NPO (site LL44-GC3) and the Japan Sea (Fig. 1). We exclusively focus on P_{auth} and P_{det} , and, consistent with previous work, assume that CFA and fluorapatite do not undergo appreciable dissolution during transport in the atmosphere – ocean system (Herut et al., 1999; Migon et al., 2001). Our calculations do not include P_{org} because uncertainty exists regarding the role of refractory organic compounds in the biogeochemical cycling of marine P (Paytan et al., 2003; Sannigrahi et al., 2006). Likewise, we do not consider P_{ox} because P_{ox} transported to the marine realm as dust and riverine sediments can desorb and enter the dissolved P pool upon interaction with saline surface waters (Berner and Rao, 1994; Herut et al., 1999; Pan et al., 2002). It is therefore unlikely that atmospheric P_{ox} accumulates within marine sediments, but we note that deposition of P_{ox} could have important implications for the cycling of dissolved P in seawater.

Bulk surface sediment at site LL44-GC3 contains 95 wt. % dust and has a P_{tot} concentration of 16 $\mu\text{mol/g}$ (Filippelli, 1997; Kyte et al., 1993). Chinese Loess contains on average 6.47 and 6.49 $\mu\text{mol/g}$ as P_{auth} and P_{det} , respectively. Using this information, we calculate that dust contributes 12.31 $\mu\text{mol/g}$ (77%) of the sedimentary P_{tot} (Table 1).

TABLE 1. DUST AND P CONCENTRATIONS IN SURFACE SEDIMENTS FROM THE NORTH PACIFIC OCEAN AND JAPAN SEA

	North Pacific Ocean	Japan Sea
Bulk surface sediment		
[Dust]	95 wt%*	24 wt% [†]
[P _{tot}]	16 µmol/g*	13 - 35 µmol/g [§]
[P _{auth}]	n.a.	3.4 - 4.6 µmol/g [§]
Contribution from dust in bulk surface sediment		
[P _{tot}]	12.31 µmol/g	3.11 µmol/g
[P _{auth}]	n.a.	1.56 µmol/g
%P _{tot}	77%	9 - 24%
%P _{auth}	n.a.	34 - 46%

Table 6.1. *. Kyte et al. (1993) and Filippelli (1997); [†]. Irino and Tada (2000); [§]. Cha et al. (2005).

This demonstrates that the vast majority of P_{tot} originates from atmospheric deposition. Although the speciation of P within these sediments is unknown, our findings further imply that a substantial fraction of P_{tot} has no relation to the marine P cycle and early diagenetic processes.

Because the Japan Sea is immediately downwind of the Chinese Loess Plateau, dust accumulation rates in the basin are high and comparable to average total mass accumulation rates (Irino and Tada, 2000; Jacobson and Holmden, 2006; Uematsu et al., 2003). A study from ODP Site 797 suggests bulk surface sediment contains 24 wt. % dust (Irino and Tada, 2000) indicating that atmospheric deposition supplies $3.11 \mu\text{mol/g}$ of P_{tot} to the sediment. Cha et al. (2005) applied SEDEX to a spatial transect of sediments from the Ulleung Basin in the Japan Sea and reported P_{tot} concentrations of $13 - 35 \mu\text{mol/g}$. Assuming surface sediments throughout the Japan Sea contain a uniform dust concentration, we estimate that dust contributes $9 - 24\%$ of the sedimentary P_{tot} (Table 1). Cha et al. (2005) also reported sedimentary P_{auth} concentrations of $3.4 - 4.6 \mu\text{mol/g}$. It follows that dust contributes $1.56 \mu\text{mol/g}$ ($34 - 46\%$) of the sedimentary P_{auth} (Table 1). This suggests that estimates of biological production, redox conditions, and the residence time of P may need revision to account for the atmospheric supply of minerals previously interpreted to form entirely *in situ*.

Cha et al. (2005) suggested that P_{auth} in Japan Sea surface sediments could precipitate at or near the sediment/water interface (SWI). Evidence cited to support this hypothesis includes the presence of P_{auth} in surface sediments and decreasing dissolved phosphate concentrations with increasing depth below the SWI. However,

this trend is not observed in all cores and when the trend is observed, no apparent increase in P_{auth} exists to suggest that authigenic phases are concomitantly incorporating phosphate.

Bottom waters of the Ulleung Basin have high dissolved oxygen concentrations (Kim and Kim, 2001). Therefore, high dissolved phosphate concentrations observed at the SWI most likely reflect high P release rates during oxidative OM decomposition. Once dissolved phosphate is released to oxygen-rich pore and bottom waters, it preferentially adsorbs to oxides and oxyhydroxides (Slomp et al., 1996a). In the cores studied by Cha et al. (2005), increasing dissolved phosphate concentrations at the SWI correlate with increasing P_{ox} concentrations, suggesting that P_{ox} is the primary sink for phosphate in these sediments. This study suggests that P_{auth} at the SWI simply originates from dust deposition.

6.5 IMPLICATIONS

Previous studies have assumed that CFA forms authigenically within shallow marine sediments as biological processes degrade OM and release associated phosphate to the dissolved pool during early diagenesis (Ruttenberg and Berner, 1993). This assumption has fostered new interpretations of C_{org}/P molar ratios in both modern and ancient depositional environments (Anderson et al., 2001) and has led to a downward revision of the residence time of P in the global ocean (Ruttenberg, 1993; Ruttenberg, 2003). Related research has suggested that the burial efficiency of P_{auth} can serve as a proxy for paleoproductivity (Schenau et al., 2005) and redox conditions (Slomp et al., 2004; Slomp and Van Cappellen, 2007). Our findings provide an important cautionary warning for these interpretations by demonstrating that a substantial fraction of P_{auth} in sediments from the NPO and its marginal seas can originate from atmospheric deposition.

Recognition of an atmospheric P_{auth} flux could help resolve enigmas surrounding the marine P cycle. For example, C_{org}/P_{react} ratios in modern oxic marine sediments rarely deviate from the Redfield ratio of 106:1. However, these observations are predicated on measurement of P within bulk marine sediments, not organic matter itself (Anderson et al., 2001 and references therein). Other sediment trap studies taking into account in-trap mineralization have demonstrated that P_{org} preferentially regenerates from organic matter throughout the water column (Clark et al., 1998; Honjo and Manganini, 1993; Loh and Bauer, 2000). Similar work conducted in the NPO and other ocean basins has shown that elevated $(C/P)_{org}$ ratios can occur across a wide range of

depths and environments, but C_{org}/P_{react} ratios remain at or near Redfield values (Faul et al., 2005). This phenomenon was attributed to precipitation of P_{auth} within the water column although a mechanism leading to P_{auth} formation was not identified. Transport of P_{auth} -bearing dust through the water column provides an alternative explanation.

A significant contribution of terrestrially derived P_{auth} to sediments within the global ocean will alter residence time estimates for dissolved P. Discovery that P_{auth} forms *in situ* led to a downward decrease in dissolved P residence time estimates from ~80 kyr (Froelich et al., 1982) to 10 – 17 kyr (Ruttenberg, 2003). These revised estimates have spurred renewed interest in the role of P as a limiting nutrient during glacial-interglacial timescales (Filippelli et al., 2007). However, if a large quantity of P_{auth} that has been observed is, in fact, being delivered from terrestrial sources, an upwards revision of the residence time may be required. Occurrence of P_{auth} in Saharan dust (Eijsink et al., 2000), also supplied to seawater in quantities similar to Chinese Loess (Duce et al., 1991), underscores this assertion. Such an increase could impact current theories connecting P delivery and P concentrations in marine surface waters (Berner and Rao, 1994; Herut et al., 1999; Migon and Sandroni, 1999) and interpretations of global climate related to the role of P as a biolimiting nutrient (Filippelli et al., 2007).

6.6 CONCLUSIONS

The atmospheric supply of P_{auth} from the Chinese Loess Plateau influences accumulation of P_{auth} in modern marine sediments of the North Pacific Ocean and the Japan Sea. This implies that studies utilizing P_{auth} in ancient marine deposits to reconstruct paleoenvironmental and paleoclimatic conditions should attempt to identify or estimate terrestrial P_{auth} sources and assess mechanisms that could have supplied P_{auth} during sedimentary deposition, including atmospheric and riverine discharge. We hypothesize this is especially important for continental shelves, where rivers could provide a substantial flux of P_{auth} depending upon the lithology of their drainage basins.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Throughout the Phanerozoic, intervals of widespread burial of organic carbon (C_{org}) –rich facies have been associated with major perturbations to the global climate system. Studies examining the mechanisms responsible for deposition of these facies have examined the competing roles conditions for enhanced preservation (Demaison and Moore, 1980), including ocean anoxia and clastic dilution, versus an enhanced flux of organic matter (OM) to marine sediments via increased rates of primary production (Pedersen and Calvert, 1990). More recently it has been suggested that ideal conditions for increased burial of OM involve both enhanced preservation as well as elevated productivity rates (e.g., Sageman et al., 2003). However, there is still much debate regarding potential sources of nutrients to marine surface waters during such events.

In this study I have utilized the SEDEX sequential extraction procedure (Anderson and Delaney, 2000; Ruttenger, 1992) to address different mechanisms of bioavailable phosphorus (P) delivery to marine surface waters during two intervals of widespread deposition of C_{org} –rich facies in the geologic past. These intervals include the Cenomanian – Turonian (C - T) Oceanic Anoxic Event (OAE) 2 and Frasnian – Famennian (F – F) biotic crisis. However, before assessing the role that variations in the marine P cycle may have had on these events, it was necessary to evaluate whether the SEDEX method provides accurate data to make such interpretations.

Chapter 2 of this dissertation examines the hypothesis that authigenic P (P_{auth}) mineral phases undergo post-burial diagenesis to less soluble forms over geologic timescales and thus can be misrepresented as detrital P (P_{det}) minerals by the SEDEX method (Filippelli and Delaney, 1995). I have demonstrated via cross plots of P_{det} versus P_{react} , however, that over a broad range of depositional environments and geologic ages such diagenesis is not evident. Rather, it can be misinterpreted as such when total P concentrations exceed a threshold value of 50 $\mu\text{mol/g}$ as a result of processes such as winnowing resulting in extraordinary concentrations of P_{auth} components such as fish debris and other phosphatic material. Based upon these observations, it is concluded that utilization of the SEDEX method provides the best currently available methodology for analysis of P cycling in ancient marine deposits.

Following those conclusions, SEDEX was applied to three sites spanning both a latitudinal and proximal transect across the C – T OAE 2 interval. The goal of this study was to assess two possible mechanisms of P delivery to marine surface waters necessary to produce the enhanced rates of primary production interpreted to be associated with this event. Results presented in Chapter 3 suggest increased terrestrial input prior to the event from deposits of the shallow marine Western Interior Seaway (WIS) and corresponding increased P_{react} accumulation in both the WIS and tropical North Atlantic. During OAE 2, following a sea-level rise event, terrestrial P delivery approaches near zero values while P_{react} accumulation is also significantly reduced in both the WIS and tropical North Atlantic. However, the WIS remains relatively oxic during the early stages of the event while deposits of the tropical North Atlantic suggest a productivity – anoxia feedback (PAF) mechanism sustaining the nutrient budget

throughout the event in the open ocean. Preliminary modeling results presented in Chapter 4 suggest that P released during oxic OM degradation in the WIS may have been sourced to the global ocean during OAE 2, perhaps due to decreased availability of Fe and other oxides and oxyhydroxides. Based upon these geochemical observations and modeling results, it is concluded that enhanced terrestrial input prior to the onset of OAE 2 preconditioned the global ocean to a state of an elevated nutrient supply. Hence primary productivity which combined with a sea-level transgression created oxygen-deficient conditions in the global ocean sufficient for a PAF mechanism to maintain the nutrient supply necessary to sustain enhanced productivity throughout the event.

A similar geochemical experiment was conducted to assess the roles of terrestrial nutrient supply versus P recycling on deposition of C_{org} –rich facies characteristic the Lower and Upper Kellwasser events deposited during the F – F biotic crisis. Here, utilization of the SEDEX method combined with previously published C_{org} , δ^{13}_{org} , and trace element data (Murphy et al., 2000a; Murphy et al., 2000b; Sageman et al., 2003) allowed for the examination of previously published hypotheses (Algeo et al., 1995; Algeo and Scheckler, 1998; Murphy et al., 2000a) pertaining to the potential sources of nutrients to marine surface waters necessary to support interpreted increased rates of primary production. In this study I present a conceptual model that accounts for the combination of observations supporting the roles of enhanced terrigenous input, sea-level rise, and a PAF mechanism all combining to result in the deposition of laminated, C_{org} –rich black shale facies characteristic of the Lower and Upper Kellwasser Horizons.

Finally, in Chapter 6 I present the first documented evidence of a terrestrial source of P_{auth} mineral phases to modern surficial marine sediments. This was accomplished via quantifying the P phases defined by the SEDEX method in Chinese Loess and then comparing these to P concentrations at two sites (the Japan Sea and North Pacific Ocean) where the concentration of eolian derived loess and either total P (North Pacific Ocean) or P_{auth} (Japan Sea) is known. Demonstrating that P_{auth} has a non-reactive, terrestrial source to marine sediments may have significant implications regarding our current estimates of the residence time of P in the global ocean as well as the usefulness of such phases as a redox and/or productivity proxy in ancient marine deposits. Thus, further work is necessary to quantify such accumulation across a range of modern environments as well as development of methodologies to assess such P phases in ancient deposits.

Overall, this study has demonstrated that studies of ancient marine nutrient budgets must consider all possible mechanisms of delivery to marine surface waters. Just as recent studies regarding the mechanisms controlling C_{org} burial have accepted that both enhanced preservation and productivity occur during periods of extraordinary accumulation, studies of nutrient cycling must now also recognize that no one mechanism can explain periods of the geologic past interpreted to have been influenced by increased rates of primary production. Future studies of the ancient marine P cycle must examine the combined effects of terrestrial fluxes as well as PAF type mechanisms to fully explain nutrient sources to the global ocean.

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APPENDIX I: P PHASE, C_{org}, AND C_{org}/P_{react} DATA – USGS #1 PORTLAND CORE

Core Depth m	P _{ox} μmol/g	P _{auth} μmol/g	P _{det} μmol/g	P _{org} μmol/g	P _{react} μmol/g	P _{tot} μmol/g	C _{org} wt. %	C _{org} /P _{react}
137.38	0.121	21.744	1.434	0.061	21.926	23.359	3.59	136
137.43	0.533	11.291	0.347	0.315	12.139	12.486	5.32	365
139.06	0.659	8.271	0.463	0.304	9.234	9.697	3.05	275
139.19	0.458	8.266	0.537	0.431	9.155	9.692	0.64	58
139.54	0.962	5.265	0.663	0.050	6.277	6.940	0.90	119
139.51	0.084	5.396	1.767	1.844	7.324	9.091	2.27	258
139.77	0.070	19.755	1.413	0.561	20.385	21.798	4.42	181
139.97	0.033	5.791	0.602	1.129	6.953	7.555	3.07	368
140.09	0.504	5.595	0.304	0.304	6.403	6.707	3.25	423
140.51	0.156	8.416	0.674	0.604	9.176	9.850	1.61	146
141.19	0.093	31.417	0.668	0.511	32.022	32.689	4.46	116
141.47	0.241	9.262	0.202	1.157	10.660	10.862	0.82	64
141.66	0.525	4.560	0.307	0.307	5.392	5.699	0.77	118
142.24	0.320	9.759	0.554	0.373	10.452	11.006	0.52	41
142.4	0.693	7.244	0.600	0.733	8.670	9.270	0.63	61
142.87	0.068	4.577	0.747	0.596	5.241	5.988	0.72	114
143.05	0.612	6.534	1.710	0.011	7.157	8.867	0.68	79
143.02	0.643	26.540	2.221	1.664	28.847	31.068	0.54	16
143.17	1.310	16.898	2.969	2.103	20.311	23.280	0.52	21
143.37	0.117	22.755	2.925	0.954	23.826	26.751	3.11	109
143.47	0.081	4.485	0.595	0.595	5.161	5.756	0.90	146
143.77	0.352	2.194	5.657	0.665	3.211	8.868	0.70	183
144.26	0.444	3.955	5.431	1.128	5.527	10.958	1.08	163
144.88	0.150	8.161	4.489	1.032	9.343	13.832	0.90	80
145.28	0.386	2.614	2.889	0.930	3.930	6.819	1.29	274
145.75	0.157	3.613	7.938	1.047	4.817	12.755	0.74	127
145.93	0.827	13.726	3.091	0.105	14.658	17.749	0.73	42
146.35	0.153	8.550	3.144	0.986	9.689	12.833	1.01	87
146.79	0.199	1.982	7.348	0.284	2.465	9.813	0.62	210
146.93	0.629	8.914	0.616	0.643	10.186	10.802	0.14	12
147.38	0.128	5.738	3.996	0.236	6.102	10.098	0.31	42
147.74	0.085	6.412	6.000	0.183	6.680	12.680	0.70	88
148.66	0.531	18.493	3.251	0.104	19.128	22.379	0.84	36
148.97	1.166	10.769	2.343	0.483	12.417	14.760	3.17	213
149.27	0.265	18.406	11.381	3.101	21.772	33.153	2.76	106
149.88	0.446	10.954	1.214	0.000	11.400	12.614	3.38	247
150.33	0.556	8.861	3.777	0.046	9.463	13.240	3.10	273
150.64	0.006	7.851	4.956	1.656	9.513	14.469	3.76	329

150.8	0.323	13.767	1.855	0.104	14.194	16.049	2.72	160
151.41	1.562	14.910	1.389	0.000	16.472	17.861	4.96	251
151.55	1.010	17.676	2.208	0.059	18.745	20.953	3.71	165
151.85	0.533	16.219	1.700	0.112	16.864	18.564	1.91	94
152.32	1.251	13.037	0.652	1.740	16.028	16.680	4.01	208
152.76	2.703	8.486	0.677	0.000	11.189	11.866	3.01	224
154	0.080	13.478	5.228	2.989	16.547	21.775	3.36	169
154.15	0.147	8.572	3.606	2.268	10.987	14.593	3.01	228
154.91	0.498	12.692	1.706	0.135	13.325	15.031	3.12	195
155.37	0.373	10.848	1.531	0.096	11.317	12.848	2.60	191
155.98	0.607	13.017	1.490	0.102	13.726	15.216	3.00	182
156.89	0.031	9.403	1.827	3.014	12.448	14.275	3.11	208
157.96	0.856	11.912	0.474	1.930	14.698	15.172	2.16	122
160.86	0.096	8.990	2.343	2.524	11.610	13.953	1.76	126
160.97	0.000	7.798	6.974	2.890	10.688	17.662	3.58	279

APPENDIX II: P PHASE, C_{org}, AND C_{org}/P_{react} DATA – RAM FALLS SECTION

Core Depth m	P _{ox} μmol/g	P _{auth} μmol/g	P _{det} μmol/g	P _{org} μmol/g	P _{react} μmol/g	P _{tot} μmol/g	C _{org} wt. %	C _{org} /P _{react}
20	0.687	16.870	4.908	0.184	17.741	22.649	0.77	36
21	0.778	17.435	3.800	0.000	18.213	22.013	1.34	61
23.5	0.916	18.537	3.997	0.000	19.453	23.450	1.72	74
25	0.847	20.261	6.310	0.135	21.243	27.553	1.19	47
26	1.093	20.562	4.258	0.181	21.836	26.094	1.01	39
27	0.906	19.434	7.756	0.000	20.340	28.096	1.85	76
28	1.248	20.359	8.348	0.000	21.607	29.955	2.50	97
28.5	0.965	19.557	9.186	0.053	20.574	29.760	2.65	107
29	0.996	17.191	7.157	0.061	18.248	25.405	2.05	94
29.8	1.009	13.379	18.161	0.072	14.460	32.621	2.11	121
30.5	1.036	18.018	7.726	0.061	19.115	26.841	1.37	60
31.5	1.027	19.309	7.624	0.041	20.377	28.001	1.85	76
32.5	1.047	16.765	7.325	0.048	17.860	25.185	2.22	104
33	1.013	17.405	8.433	0.056	18.474	26.907	2.32	105
34	1.021	16.497	9.481	0.057	17.575	27.056	2.64	125
36	1.026	20.244	5.862	0.056	21.325	27.187	2.49	97
37.5	1.028	23.397	4.835	0.053	24.478	29.313	2.45	83
39	1.027	18.648	8.378	0.052	19.727	28.105	3.05	129
40	1.027	24.074	3.203	0.054	25.155	28.358	2.77	92

APPENDIX III: P PHASE, C_{org}, AND C_{org}/P_{react} DATA – ODP SITE 1258

Core Depth m	P _{ox} μmol/g	P _{auth} μmol/g	P _{det} μmol/g	P _{org} μmol/g	P _{react} μmol/g	P _{tot} μmol/g	C _{org} wt. %	C _{org} /P _{react} t
420.65	0.581	24.18	0.786	0	24.761	25.547	11.65	392
420.85	0.954	37.671	0.313	0.489	39.114	39.427	9.26	197
420.89	0.778	27.541	1.286	0	28.319	29.605	13.20	388
421.3	0.168	13.566	0	0	13.734	13.734	3.84	233
421.44	0.679	30.923	0.446	0.113	31.715	32.161	6.48	170
421.57	0.765	18.597	0.39	0	19.362	19.752	8.22	354
422.27	0.929	24.225	1.953	0	25.154	27.107	24.10	798
422.51	2.339	24.82	4.945	0	27.159	32.104	18.68	222
422.78	1.195	77.873	35.28	1.953	81.021	116.301	14.50	149
423	0.206	30.562	4.632	0	30.768	35.400	21.36	579
423.2	0.437	20.245	0.474	0.755	21.437	21.911	7.37	287
423.37	0.478	7.458	1.471	0	7.936	9.407	17.25	1811
423.79	0.181	7.396	1.615	0	7.577	9.192	3.82	430
423.98	0.477	37.506	8.55	0	37.983	46.533	6.18	137
424.3	0.766	9.825	0	0.487	11.078	11.078	5.71	429
424.45	0.783	6.851	1.127	0.078	7.712	8.839	22.60	2749
424.84	0.109	13.779	2.034	0.043	13.931	15.965	20.62	1233
424.85	0.377	7.926	0	0	8.303	8.303	15.10	1588
425.05	0.573	9.046	1.227	1.356	10.975	12.202	3.59	273
425.18	0.445	5.161	1.719	0	5.606	7.325	19.00	3068
425.52	1.789	27.967	0.016	0.296	30.052	30.068	5.79	160
425.63	0	6.506	0.033	0	6.506	6.539	15.00	318
425.73	0.327	31.149	0.014	0.283	31.759	31.773	12.00	637
425.98	2.032	93.178	57.351	4.407	99.617	156.968	13.98	74
426.2	0.104	11.802	0.519	1.057	12.963	13.482	9.10	637
426.28	0.229	31.438	0.6	1.007	32.674	33.274	9.30	247
426.31	1.18	23.921	1.89	0.004	25.105	26.995	9.30	309
426.66	0.997	92.924	1.931	1.126	95.047	96.978	10.70	94
426.72	2.276	110.497	33.005	0.000	112.773	145.778	11.40	84
426.8	1.889	101.732	31.097	1.267	104.888	135.985	8.35	66
426.89	1.383	3.76	0.412	0.000	5.143	5.555	4.60	745
426.9	1.048	13.133	0	2.022	16.203	16.203	6.87	354
427.13	0.621	3.663	0	0.000	4.284	4.284	4.02	782
427.48	0.416	4.219	0	0.058	4.693	4.693	7.34	1450
427.62	0.319	15.146	1.545	0.000	15.465	17.010	3.16	174

428.1	3.754	75.498	14.679	0.000	79.252	93.931	12.50	131
428.25	0.355	20.428	0.754	0.019	20.802	21.556	12.30	493
428.57	4.477	102.609	74.129	5.183	112.269	186.398	11.70	87
428.69	0.693	53.643	0	0.877	55.213	55.213	13.30	207
428.91	2.549	138.777	59.656	1.023	142.349	202.005	8.23	48
429.14	0.117	25.001	0.337	1.184	26.302	26.639	7.07	236
429.35	0.583	98.655	3.199	1.381	100.619	103.818	10.40	86
429.41	0.429	49.328	0.021	1.611	51.368	51.389	10.40	176
430.01	1.907	131.092	53.476	1.325	134.324	187.800		
430.1	1.357	68.392	17.116	0.000	69.749	86.865		
430.17	0.003	3.772	0	1.229	5.004	5.004	0.70	155
430.39	3.737	148.982	82.336	0.000	152.719	235.055	9.51	52
430.43	0.099	74.08	0	1.007	75.186	75.186		
430.92	1.578	9.546	0.49	0	11.124	11.614	22.36	1675
430.98	1.65	32.348	0.442	1.994	35.992	36.434	9.44	219

APPENDIX IV: P PHASE, C_{org}, AND C_{org}/P_{react} DATA – NX-1 WEST VALEY CORE

Core Depth m	P _{ox} μmol/g	P _{auth} μmol/g	P _{det} μmol/g	P _{org} μmol/g	P _{react} μmol/g	P _{tot} μmol/g	C _{org} wt. %	C _{org} /P _{react}
234.55	1.038	11.063	6.729	8.896	20.997	27.725	0.56	22
235.2	0.407	11.093	2.818	5.345	16.845	19.664	0.31	15
235.5	0.650	13.073	4.318	4.557	18.280	22.598	0.25	11
235.8	0.091	4.101	4.109	1.414	5.607	9.715	0.26	39
236.1	1.086	5.230	8.392	3.670	9.986	18.378	3.22	269
236.49	0.565	1.973	9.176	1.663	4.201	13.378	3.65	724
236.84	0.440	2.279	7.168	2.868	5.587	12.755	2.63	392
237	0.516	3.025	6.514	2.711	6.252	12.766	2.94	392
237.24	0.282	2.730	7.761	1.915	4.928	12.688	2.56	433
237.64	0.337	3.159	8.958	2.508	6.003	14.961	0.13	18
238.02	0.411	2.545	10.987	3.999	6.955	17.942	0.37	44
238.74	0.166	4.121	6.086	4.620	8.907	14.993	0.47	44
239.14	1.250	4.735	6.982	4.289	10.274	17.255	1.86	151
239.89	0.431	4.820	4.416	5.202	10.454	14.870	0.50	40
240.96	0.444	4.608	4.176	4.923	9.975	14.151	0.63	53
241.98	0.444	2.337	2.972	4.078	6.859	9.831	0.22	27
243.34	0.534	10.047	3.502	4.837	15.418	18.920	0.43	23
244.53	0.639	3.703	2.808	3.456	7.798	10.606	1.78	190
272.19	1.25	3.28	4.70	2.19	6.724	11.427	0.29	36
273.06	1.10	5.54	2.00	2.92	9.558	11.560	0.3	26
274.3	1.04	3.45	1.21	3.99	8.486	9.691	0.2	20
274.55	0.90	5.31	1.38	4.02	10.225	11.607	2	163
274.7	1.28	5.01	2.85	2.39	8.679	11.530	3.21	308
274.79	1.90	4.79	4.38	3.07	9.765	14.148	3.53	301
274.93	0.99	12.46	2.75	2.99	16.443	19.195	0.47	24
275.32	0.77	3.05	3.96	5.03	8.852	12.814	5.03	474
275.84	0.53	4.78	2.19	0.86	6.174	8.368	3.43	463
276.13	0.74	6.80	3.38	4.21	11.752	15.128	3.17	225
276.43	0.96	2.34	2.49	3.11	6.409	8.902	4.75	618
276.8	0.65	5.44	3.37	2.98	9.078	12.450	5.19	476
277.09	0.93	2.72	2.95	3.58	7.233	10.184	3.24	373
277.25	0.53	4.60	3.01	3.70	8.837	11.845	5.14	485
277.85	0.97	3.70	5.02	3.96	8.637	13.660	2.58	249
278.16	0.25	8.99	3.69	2.71	11.946	15.636	1.54	107
278.49	1.04	3.99	2.70	7.05	12.080	14.784	0.62	43
278.73	0.44	6.07	4.58	5.76	12.267	16.847	2.47	168

279.23	1.24	11.71	7.13	4.11	17.063	24.193	0.66	32
279.86	0.60	8.31	4.81	2.00	10.906	15.715	1.06	81
280.5	0.53	4.11	2.70	6.94	11.584	14.284	0.54	39
280.8	1.14	9.69	3.11	2.80	13.627	16.735	0.89	54
281.96	0.90	3.54	1.79	6.19	10.626	12.412	0.51	40
283.17	1.01	5.21	2.37	4.80	11.013	13.380	0.12	9

APPENDIX V: P CONCENTRATIONS IN CHINESE LOESS SAMPLES

Sample	P _{sorb} μmol/g	P _{ox} μmol/g	P _{auth} μmol/g	P _{det} μmol/g	P _{org} μmol/g	P _{tot} μmol/g
BinXian Li4	1.801	0.273	7.972	4.844	0.31	15.2
Binxian Li1	0.527	1.293	6.901	5.933	0.363	15.017
Lan Tian Li1	2.092	0.671	5.953	7.493	0.132	16.341
Lan Tian Li4	2.123	0.602	4.847	2.861	0.306	10.739
MuBo Li1	0.479	1.15	6.185	9.949	0.174	17.937
MuBo Li4	1.115	0.552	2.671	7.495	0.281	12.114
NingXian Li4	1.523	0.548	10.063	6.07	0.311	18.515
NingXian Li1	0.18	1.126	7.331	7.041	0.37	16.048
Qing Yang Li1	1.516	0.609	4.221	8.189	0.332	14.867
QingYang Li4	0.609	1.089	8.552	5.025	0.465	15.74

VITA

Jason Flaum was born in West Islip, NY on August 27, 1976. He received his B.S. from the University of Miami in Marine Science and Geology in May, 1998 and his M.S. from the University of Alabama in Geology in December, 2003. Now he is embarking on a career as a geoscientist for the energy industry and most looking forward to being a proud father for years to come.