

Multi Isotope Study Of The Cenomanian- Turonian Ocean Anoxic Event 2 Of The Eagle Ford
Formation Of West Texas

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DEDICATION

This dissertation is dedicated to both my grandmothers

Yvette Ngatchou Espe Nana

and

Late Emilia Noumen

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ABSTRACT

Ocean anoxic events (OAEs) are periods in the geologic past where the Earth's global ocean becomes depleted in oxygen. These events resulted in strong biogeochemical changes within ocean basins and are amongst the largest climatic perturbations in the Phanerozoic. The OAEs resulted in increased ocean productivity, although the mechanisms that sustained such long periods of anoxia (~100- 900 kyr) remain poorly understood. In this study, a careful dissolution is used to access the carbonate fractions of core samples from the Late Cretaceous Eagle Ford Group and Buda Limestone of West Texas. This study, through the measurement of $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{88/86}\text{Sr}$, $\delta^{44/40}\text{Ca}$ and $\delta^{53}\text{Cr}$, focused on the Cenomanian – Turonian Ocean Anoxic event (OAE 2), to understand the biogeochemical mechanisms that were governing the global ocean during this period of anoxia.

Results show that seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios change synchronously with Os isotopes for the onset of massive LIP volcanism, and 60 kyr before the positive C isotope excursion that traditionally marks the onset of OAE 2. Using an ocean Sr box model, it is found that increasing the continental weathering Sr flux by ~1.8-times captures the change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ recorded in the Iona-1 core. The increase in the continental weathering flux is smaller than the threefold increase suggested by studies of seawater Ca and Li isotope changes during OAE 2, suggesting that hydrothermal forcing may have played a larger role in the development of ocean anoxic events than previously considered. The increasing role of hydrothermal forcing resulted in a negative carbonate $\delta^{53}\text{Cr}$ profile through OAE 2 of the Iona-1 core. Importantly, the decrease in the $\delta^{53}\text{Cr}$ occurs ~70 kyr after the drop in initial $^{187}\text{Os}/^{188}\text{Os}$ that marks the onset of LIP activity, continuing to highlight the significance of hydrothermal activity during this time. The $\delta^{44/40}\text{Ca}$ on the other hand, shows a positive

excursion through OAE 2, punctuated by intervals of high values interpreted to have resulted from syn-depositional diagenesis as a result of nutrient upwelling, thereby highlighting hydrothermal interaction. Overall, the results show that increased LIP activity played a significant role during OAE 2.

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INTRODUCTION

Ocean anoxic events (OAEs) are periods in the geologic past when the Earth's global ocean became depleted in oxygen. Stages in the Mesozoic where OAEs have been identified in stratigraphic sections include the Toarcian Stage in the Jurassic Period, and the Aptian, Albion, and Cenomanian – Turonian Stages in the Cretaceous Period. These events, which lasted from 250 kyr to as much as 900 kyr, resulted in strong biogeochemical changes within the oceans and are amongst the largest climatic perturbations in the Phanerozoic (Schlanger and Jenkyns 1976; Sageman et al., 2006; Eldrett et al., 2014). The OAEs are identified by widespread deposition of marine black shales where unusually large amounts of organic carbon were deposited in marine sediments. These black shales were interpreted to represent periods of prolonged anoxia, possibly linked to expanded oxygen minimum zones (Jenkyns, 2010). Subsequent identification of other occurrences of OAEs proved to be problematic, as diagenesis and local expressions of the events vary from location to location, making the stratigraphic expression non-uniform (Tikos et al., 2004). Hence, criteria other than the occurrence of black shales, such as from significant positive shifts in both organic and carbonate $\delta^{13}\text{C}$ values, have been used to identify these events.

The causal mechanism of OAEs and how increased ocean productivity can be sustained for periods of 100,000s of years are still poorly understood. Many view these events as a climatically driven response to increased nutrient availability, triggered by volcanic activity and emplacement of large igneous provinces (LIPs) such as the Caribbean and Arctic igneous provinces in the Late-Cretaceous (Larson and Erba, 1999). These LIPs likely released large quantities of CO_2 and hydrothermally sourced iron in the

photic zone, driving primary productivity (Tikos et al., 2004; Jenkyns 2010; Pogge von Strandmann et al., 2013). Others argue the OAEs were triggered by an increase in chemical weathering on the continents as a feedback from increasing $p\text{CO}_2$ (Sinton and Duncan, 1997; Kerr, 1988; Jones and Jenkyns, 2001).

Despite the controversy surrounding the cause of the OAEs, it is agreed that, during these periods of ocean anoxia, the Earth was characterized by extreme greenhouse gases, with estimates of atmospheric $p\text{CO}_2$ as high as ~2000 ppm compared to modern values of ~400 ppm (Jenkyns 2010 and references therein). As a result, possible chains of events have been suggested rather than just one particular event to trigger an OAE. They include increased atmospheric $p\text{CO}_2$ from the emplacement of the Caribbean, Madagascar and/or parts of the Ontong-Java Plateau LIPs, which led to enhanced continental weathering and associated high nutrient input to the oceans, stimulating biological productivity and accelerated organic carbon flux to the sea floor, thus fostering the OAE (e.g., Pogge von Strandmann et al., 2013; Clarkson et al., 2018).

The timing and rates of continental weathering, which would increase as atmospheric $p\text{CO}_2$ levels increase, is critical to understanding the formation and evolution of OAEs. Additionally, since OAEs involve the widespread development of oxygen-deficient water masses, many redox-sensitive isotope systems were potentially perturbed in the global ocean during these intervals. Hence, developing records of isotopic proxies that are sensitive to changes in weathering, hydrothermal activity, and redox conditions, within a well-constrained age model, are crucial to better understand the mechanisms that create and drive OAEs.

The Cenomanian Ocean Anoxic Event 2 (OAE 2) lasted about 1 million years, from 95.1 to 93.97 Ma (Eldrett et al. 2014, 2015a, 2015b, 2017). During this time interval, there was not only a sustained period of high atmospheric $p\text{CO}_2$ and consequent warming of the global climate, but also an interval of cooling, known as the Plenius Cold Event, lasting for around 350,000 years with a short warming interval within it (Jenkyns et al., 2017). How these cooling intervals affected continental weathering, and whether they were triggered by reduced volcanic activity and consequent reduction of atmospheric $p\text{CO}_2$, remain open questions. Hence, stratigraphic sections of OAE 2 provide an ideal opportunity to examine the interplay between the factors that lead to warming and cooling of the Earth's global climate.

To date, while many stratigraphic sections through OAE 2 have been examined, comprehensive petrological and geochemical data are limited for any given section. This is because of the difficulties and enormous amounts of time to (1) obtain lithological characterization of a section followed by (2) obtaining a comprehensive set of geochemical data and production of a robust numerical model to stimulate the event. In addition, OAE 2 has only been recognized for three decades, and the geochemistry of representative stratigraphic sections are only beginning to be comprehensively examined (Schlanger et al., 1987, Clarke and Jenkyns, 1999, McArthur et al., 2004, Frijia and Parente, 2008, MacLeod et al., 2008, Turgeon and Creaser, 2008, Jenkyns, 2010, Montoya-Pino et al., 2010, Kuroda et al., 2011, Martin et al., 2012, Pogge von Strandmann et al., 2013, Zheng et al., 2013, Blättler et al., 2012, 2014; Blättler and Higgins 2014; Du Vivier et al., 2014, Holmden et al., 2016). The geochemical records from these previous studies were collected from multiple sites, which can make

comparisons challenging. Recent investigations of OAE 2 successions have focused on newly developed isotopic proxies for paleoenvironmental conditions. Hence, we are only now beginning to fully examine these sections and apply all of the possible tools to them to better understand what factors lead to ocean anoxia and associated global climate change.

My dissertation focuses on the examination of the complete stratigraphic section through OAE 2 at high temporal resolution with the aim of understanding the chemical mechanisms and biogeochemical processes that were governing the marine environment during this period of anoxia. Specifically, on determining the rate and impact of continental weathering over this interval and its relationship to redox conditions. This will be achieved through the isotopic proxies of radiogenic and stable Sr, Ca, and Cr of carbonate fractions from the Late Cretaceous Eagle Ford Group of West Texas recorded in the Iona-1 drill core. The carbonate fractions are targeted for this study because carbonates are sensitive indicators of ocean chemistry and provide a valuable record of the conditions from which they were precipitated. These new results will form a comprehensive data set that will complement previous characterization of this time interval of OAE 2. Each of these isotope proxies can individually provide distinct constraints on volcanic input, continental weathering, and ocean redox chemistry as OAE 2 progressed. I will draw on this comprehensive dataset for the Iona-1 core, with comparisons to geochemical records from other OAE 2 sections, to model the potential inputs and outputs of volcanic activity and continental weathering sources to the global ocean during this time interval. This comprehensive approach will hence provide a framework for further examination of the causes of ocean anoxia in the geological past

and will also allow for better understanding of the factors that may occur in the near future as more CO₂ is added to our atmosphere.

This dissertation is organized as a series of three manuscripts separated into three chapters formats that would/have be submitted for peer reviewed journal publication.

CHAPTER 1: CHANGING INPUTS OF CONTINENTAL AND SUBMARINE WEATHERING SOURCES OF SR TO THE OCEANS DURING OAE 2

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1.1 Abstract

Ocean anoxic events (OAE) are characterized by increased organic content of marine sediment on a global scale with accompanying positive excursions in sedimentary organic and inorganic $\delta^{13}\text{C}$ values. To sustain the increased C exports and burial required to explain the C isotope excursion, increased supplies of nutrients to the oceans are often invoked during ocean anoxic events. The potential source of nutrients in these events is investigated in this study for Oceanic Anoxic Event 2, which spans the Cenomanian-Turonian boundary. Massive eruptions of one or more Large Igneous Provinces (LIPs) are the proposed trigger for OAE 2. The global warming associated with volcanogenic loading of carbon dioxide to the atmosphere has been associated with increased continental weathering rates during OAE 2, and by extension, enhanced nutrient supplies to the oceans. Seawater interactions with hot basalts at LIP eruption sites can further deliver ferrous iron and other reduced metals to seawater that can stimulate increased productivity in surface waters and increased oxygen demand in deep waters. The relative importance of

continental and submarine weathering drivers of expanding ocean anoxia during OAE 2 are difficult to disentangle. In this paper, a box model of the marine Sr cycle is used to constrain the timing and relative magnitudes of changes in the continental weathering and hydrothermal Sr fluxes to the oceans during OAE 2 using a new high-resolution record of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios preserved in a marl-limestone succession from the Iona-1 core collected from the Eagle Ford Formation in Texas. The results show that seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios change synchronously with Os isotope evidence for the onset of massive LIP volcanism 60kyr before the positive C isotope excursion that traditionally marks the onset of OAE 2. The higher temporal resolution of the seawater Sr isotope record presented in this study warrants a detailed quantitative analysis of the changes in continental weathering and hydrothermal Sr inputs to the oceans during OAE 2. Using an ocean Sr box model, it is found that increasing the continental weathering Sr flux by 1.8 to 1.85-times captures the change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ recorded in the Iona-1 core. The increase in the continental weathering flux is smaller than the threefold increase suggested by studies of seawater Ca and Li isotope changes during OAE 2, suggesting that hydrothermal forcing may have played a larger role in the development of ocean anoxic events than previously considered

1.2 Introduction

Ocean Anoxic Events (OAE) are identified in the rock record by elevated concentrations of organic matter in marine sediments and positive shifts in sedimentary $\delta^{13}\text{C}$ values, a signal major perturbation to the Earth's exogenic C cycle from increased organic carbon burial (Schlanger and Jenkyns 1976; Sageman et al., 2006). One of the most studied examples is Ocean Anoxic Event 2 (OAE 2) spanning the Cenomanian-Turonian

boundary (CTB) in the Late Cretaceous. The duration of OAE 2 is 600,000 - 800,000 years based on rhythmically bedded strata in the Western Interior Seaway (WIS) of North America (Sageman et al., 2006; Eldrett et al., 2015a; Jones et al., 2020). Traditionally, the length of the event is represented by the stratigraphic thickness of the positive $\delta^{13}\text{C}_{\text{org}}$ excursion (CIE) of 2 to 5‰ (Scholle and Arthur 1980; Jenkyns, 2010). Two factors contribute to increased organic carbon burial: (1) higher preservation at the sediment water interface, which is enhanced during periods of expanded bottom water anoxia in the oceans (e.g., Ostrander et al., 2017), and/or (2) increased exports of primary produced organic matter from the photic zone, which is improved during periods of increased nutrient availability in the oceans (Jenkyns, 2010 and references therein). The relative importance of these two processes for OAE 2 is a frequent subject of study and debate (Blättler et al., 2011; Pogge von Strandmann et al., 2013; Owens et al., 2018; Them et al., 2018). Climate and ocean circulation models generally invoke increased continental weathering during OAE 2 as a key global change variable (e.g., Topper et al., 2011; Monteiro et al., 2012; Baroni et al., 2014) and are parameterized with continental weathering proxy studies, notably Ca and Li isotopes, to set the magnitude of the continental weathering (Blättler et al., 2011; Pogge von Strandmann et al., 2013). However, the proposed threefold increase in continental weathering fluxes of Ca to the oceans during OAE 2 proposed by Blättler et al. (2011) was based on Ca isotope records that could not be reproduced in a follow-up study by Du Vivier et al. (2015). The source and relative weight of increased supplies of nutrients to the oceans during OAE 2 is the subject of this study.

Early studies of OAE 2 (Schlanger and Jenkyns 1976; Demaison and Moore, 1980; Pedersen and Calvert, 1990) focused on climate and ocean circulation changes to explain

increased total organic carbon (TOC) concentrations in marine sediments, highlighting the role of warmer Late Cretaceous climates and sluggish circulation may have played in the preservation and burial of marine organic matter. Warmer temperatures cause increased soil mineral weathering, resulting in increased weathering supplies of nutrients to the oceans that could then fuel additional productivity, organic carbon export, increased oxygen utilization in deep waters, and expanded bottom water anoxia—thereby leading to organic carbon burial (Schlanger and Jenkyns 1976; Demaison and Moore, 1980; Pedersen and Calvert, 1990). These studies, however, could not adequately account for the timing of OAE 2 before the evidence began to grow for its volcanic origin.

Increased submarine volcanism during OAE 2 is supported by episodic increases in trace metal abundances of basaltic affinity in carbonate sediments from the proto-North Atlantic region (Orth et al., 1993). The metal source was initially attributed to increased hydrothermal venting at mid-ocean ridges (Orth et al., 1993), but was quickly amended to massive submarine eruptions of one or more Large Igneous Provinces (LIPs), particularly the Caribbean Large Igneous Province (CLIP) in the eastern Pacific, which erupted near the Central American Gateway to the proto-North Atlantic Ocean (Sinton and Duncan, 1997). A submarine volcanic trigger is further supported by a global decrease in global seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2, and similar patterns for the other Cretaceous OAEs (Ingram et al., 1994; Bralower et al., 1997; Jones and Jenkyns 2001; Ando et al., 2009). The perturbations in the ocean Sr cycle offered a means by which the magnitude of the eruptions and the volumes of seawater that interacted with hot basalt during LIP magmatic activity could be assessed (Ingram et al., 1994). However, the response of the ocean Sr cycle to the volcanic trigger was expected to be sluggish on account of the long modern

oceanic Sr residence time (2.5 Ma; Hodell et al., 1989), adjusted to 1.35 Myr in this study using updated continental input Sr fluxes from Peucker-Ehrenbrink and Fiske (2019). The poorly resolved record of changing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in the Late Cenomanian and early Turonian challenged the ability to more definitively determine shifts to the Sr cycle. Moreover, there were competing effects to the ocean Sr mass balance needs to be considered—most notably the higher continental weathering fluxes of Sr to the oceans that would drive the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater in the opposite direction to that produced by increased volcanism on the ocean floor.

In contrast to Sr, the marine Os cycle shifted very abruptly from a continental weathering-dominated signature to a mantle-dominated signature, consistent with a massive magmatic event near the onset of OAE 2 (Turgeon and Creaser, 2008; DuVivier et al., 2014; Sullivan et al., 2020; Jones et al., 2020). With its much shorter ocean residence time (3–50 kyr; Oxburgh 2001) compared to Sr (~1.35 Myr) the eruptions could be shown to have started *ca.* 20–60 kyr before the positive CIE and the onset of OAE 2. However, the LIP-induced ocean Os cycle perturbation was so large that it completely overwhelmed any increase in continental weathering of Os to the oceans that may have also occurred in response to global warming driven by volcanogenic carbon dioxide emissions.

The relative importance of continental weathering and submarine volcanic delivery of nutrients to the oceans during OAE 2, and the time scales over which they played a role in its development, remain open questions, but can be partially constrained by strontium isotope records. This is because evolution of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ reflects changes in two principle input Sr fluxes to the oceans: (1) venting of hydrothermal fluids from active submarine volcanism that deliver basaltic-derived micronutrients (Fe, Mn, Cu, Co, Zn) and

Sr with a modern $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ~ 0.7031 (Snow et al., 2005), and (2) rivers and groundwater draining the continental crust that delivers the important macronutrient, phosphate, to the oceans and Sr with a modern $^{87}\text{Sr}/^{86}\text{Sr}$ that has been estimated at 0.7110 (Palmer and Edmond 1989; Richter et al., 1992). The latter has been recently adjusted to 0.71040 to reflect the most recent comprehensive study of continental sources of Sr to the oceans (Peucker-Ehrenbrink and Fiske, 2019). The higher $^{87}\text{Sr}/^{86}\text{Sr}$ of the continental weathering input reflects the higher $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of the continental crust. Its older rock ages and higher Rb concentrations yield higher production rates of ^{87}Sr from radioactive decay of ^{87}Rb , compared to the mantle-source region (0.7025–0.7037) that melts to produce the oceanic crust (Wickman, 1948). Using simple mixing and the present-day seawater $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7092 (Elderfield, 1986), modern Sr input fluxes to the oceans from continental weathering and submarine weathering by hydrothermal fluids is estimated at 84% and 16%, respectively. The relative size of the inputs has changed over geological time. Periods of increased mountain building correlate with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of seawater while periods of rapid seafloor spreading and LIP eruptions correlate with lower ratios (Palmer and Edmond 1989; Richter et al., 1992). Carbonates of igneous and metamorphic origin in mountain uplift regions can also deliver large quantities of Sr to the oceans with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Derry and France-Lanord 1996; Jacobson et al., 2002).

Documented decreases in carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during OAE 2 suggests that submarine hydrothermal inputs were a more dominant factor than increased continental weathering inputs (Ingram et al., 1994; Bralower et al., 1997; Jones and Jenkyns 2001; Snow et al., 2005). A seawater $^{87}\text{Sr}/^{86}\text{Sr}$ record for OAE 2 that is more precise and of higher temporal resolution than those currently available (Ando et al., 2009) could help to quantify

the relative change in the Sr inputs. To address this issue, a new high-resolution record of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for OAE 2 is presented in this paper from the Iona-1 core (Eldrett et al., 2014; Minisini et al., 2018), which samples a succession of pelagic marine carbonates from the Eagle Ford Formation in Texas. A forward box model of the ocean Sr cycle is implemented in combination with a conceptual model of how continental weathering and hydrothermal inputs of Sr likely would have responded to a massive episode of LIP volcanism. The result is an estimate for the continental weathering flux increase of Sr to the oceans during OAE 2 (and by inference Ca and nutrients) that is smaller than previous estimates (Blättler et al., 2011; Pogge von Strandmann et al., 2013).

1.3 Geologic Setting

The Iona-1 core was drilled on a carbonate shelf at the southern gateway to the WIS in present-day southwest Texas (29°13.51'N, 100°44.49'W). The core recovered 180 m of Lower Cenomanian to Lower Coniacian marine sediment composed of marls and shales, with intermittent bentonite of the Boquillas Formation of the Eagle Ford Group (Eldrett et al., 2014). Sedimentation was slow and assumed to be relatively continuous during OAE 2 in the study setting (Eldrett et al., 2015a). An age model for the Iona-1 core was constructed from rhythmically deposited inter-bedded limestones and marlstones that were interpreted to reflect orbitally forced on sedimentation patterns and is supported by U-Pb zircon dating of bentonite beds (Eldrett et al. 2014, 2015a, 2015b; Minisini et al., 2018). The interbedded marls are predominantly finely laminated and organic-rich in the lower Eagle Ford and become more bioturbated up core (Eldrett et al., 2014). Stratigraphic patterns in the traces of burrowing organisms and the diversity of benthic foraminifera documented periods of

alternating oxic to dysoxic and anoxic bottom waters in the study area during OAE 2. Intervals of organic-rich laminated sediment and elevated trace metal nutrients are associated with bottom water anoxia (Eldrett et al., 2014; 2015a and Minisini et al., 2018). The depth of deposition is interpreted to be consistently below storm wave base in a restricted, sediment-starved setting (100 to 200 m depth; Eldrett et al., 2014). The decrease in initial $^{187}\text{Os}/^{188}\text{Os}$ (Sullivan et al., 2020) begins ~60 kyr prior to the onset of the positive C isotope excursion that traditionally marks the base of OAE 2 and, consistent with recently published Os isotope evidence supporting the volcanic trigger hypothesis for OAE 2 (DuVivier et al., 2014, Jones et al., 2020). The carbonate fraction of the sediment is mostly original low magnesium calcite mud derived from planktic foraminifera and calcispheres. Further details on the sedimentology, stratigraphy, and hydrographic conditions can be found in Eldrett et al., (2014, 2015a, 2017) and Minisini et al. (2018).

1.4 Analytical Techniques

1.4.1 Sample dissolution

Samples were collected approximately every 25 cm for Sr isotope analysis in the study interval of the core. The mixed limestone-marlstone-siliciclastic lithology of the Iona-1 core makes it important to use an acid that will dissolve carbonate minerals precipitated from seawater but will not appreciably attack and release Sr from non-carbonate minerals with higher or lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The dissolution procedure employed in this study has two sequential steps: (1) an ammonium acetate wash to remove Sr from exchange sites on clays and broken mineral surfaces from grinding, and (2)

dissolution of the carbonate fraction of the sediment in buffered acetic acid (e.g., Bailey et al., 2000; Li et al., 2011).

In detail, 5 mL of 1 M ammonium acetate solution was added to 200 mg of rock powder for 12 hours after which sample was centrifuged, the supernatant decanted, and the sample rinsed three times with ultrapure water. The samples were then immersed in 5 mL of 1 M buffered Optima glacial grade acetic acid for 1–2 hours at room temperature to dissolve carbonate minerals. The leachate was separated from the residue by centrifugation. The solution was then dried down and the acetate removed by redissolving the sample in a few mL of 6 N nitric acid (HNO_3) and dried down again. This step was repeated three times to ensure that acetate was decomposed. The residues were then dissolved in 0.45 N HNO_3 and transferred to pre-weighed acid-cleaned 50 mL centrifuge tubes. An aliquot of the stock solution was used for the analysis of elemental concentrations by inductively coupled plasma mass spectrometry (ICPMS) and inductively-coupled optical emission mass spectrometry (ICP-OES). Another aliquot was passed through a column containing Eichrom Sr Spec resin to purify Sr from Ca and other matrix elements prior to mass spectrometric analysis using thermal ionization mass spectrometry (TIMS).

1.4.2 Analytical techniques

Major and trace element concentrations were determined by ICP-OES and ICP-MS, respectively, at the University of Houston. Analytical uncertainty is generally better than $\pm 5\%$ 1σ , monitored by repeated analysis of an internal standard. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured using a Thermo Scientific Triton Plus TIMS at the University of Houston using a multi-static measurement technique adapted from a method for obtaining

high precision Nd isotopic ratios (Bennett et al., 2007). The measurement procedure begins with a slow increase of the filament temperature during which time the Sr ion beams are located, tuned, and peak-centered multiple times until a stable ^{88}Sr ion beam intensity of 6V is reached. Three sets of Sr isotopic ratios were collected in each cycle (3 scans), with 10 cycles per block and 14 blocks per run, for a total of 420 measurements of $^{88}\text{Sr}/^{86}\text{Sr}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{84}\text{Sr}/^{86}\text{Sr}$. Mass 85 was monitored to correct $^{87}\text{Sr}/^{86}\text{Sr}$ for ^{87}Rb interference, but Rb beams were too small to warrant any significant corrections. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were corrected for instrumental mass fractionation using a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194.

The external precision for $^{87}\text{Sr}/^{86}\text{Sr}$ is ± 5 ppm (2σ) based on repeated measurements of the SRM 987 standard yielding $0.710251 \pm 2.951\text{E-}06$ ($n=20$) over the course of this work.

1.5 Results

1.5.1 Elemental concentrations

Trace element concentrations were used to screen the leachates for non-carbonate sources of Sr by monitoring co-release of Al and Rb that are high in detrital clay minerals but low in marine carbonates (Tribovillard et. al., 2006). The low Al concentrations (average ~ 200 ppm) in the leachates indicate that the ammonium acetate rinse of the sample powders and the weak acetic acid used to dissolve carbonate minerals resulted in a very minor release of Al from the samples. The Al concentrations in the leachates are consistent with those of modern pure carbonate sediments where the main source of Al is from seawater itself (Veizer, 1983). As a point of comparison, Veizer (1983) reports 4600 ppm Al in pure marine carbonates, which is higher than concentrations measured in this study,

and much lower than concentrations of ~80,000 ppm in shales. The low Al concentrations in the sample leachates is strong evidence for negligible release of Sr from non-carbonate minerals.

Manganese can also reside in metalliferous coatings on sediment grains. Although the concentration of Sr is insignificant in these coatings (Veizer, 1983), sample leachates with elevated Mn concentrations may still record seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Higher Mn concentrations in carbonates deposited in the proto-North Atlantic region during OAE 2 (Pratt et al., 1991) reflect higher oceanic inventories of Mn, due to the reduction in the size of the oxic marine sink where Mn-oxides would have normally accumulated, and increased Mn fluxes from hydrothermal weathering of the LIP basalts (Orth et al., 1993; Sinton and Duncan, 1997; Snow et al., 2005). However, the Mn concentrations recorded in the carbonate fractions of the Iona-1 core are relatively low.

1.5.2 Sr isotopes

The carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ profile in the Iona-1 core is a smoothly varying function of stratigraphic depth (Fig. 1.1 and listed in Table 1.1). This meets the expectation for a sedimentary succession with no major depositional hiatuses, for an element like Sr with a long oceanic residence time. The overall trend is one of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 followed by a decreasing trend in the early part of OAE 2, a period of no change in $^{87}\text{Sr}/^{86}\text{Sr}$ in the middle part of OAE 2, and a resumption of the declining trend in $^{87}\text{Sr}/^{86}\text{Sr}$ for the remainder of OAE 2. In detail, the shift from increasing to decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios near the onset of OAE 2 occurs at the same stratigraphic level as the decrease in $^{187}\text{Os}/^{188}\text{Os}$ ratios signaling the massive increase in LIP volcanism. The ~ 150 kyr of no change in

$^{87}\text{Sr}/^{86}\text{Sr}$ occurs in a stratigraphic interval marked by the beginning of the post-volcanic rise in oceanic $^{187}\text{Os}/^{188}\text{Os}$ ratios, and the end of the peak positive shift in sedimentary $\delta^{13}\text{C}$ values (Fig. 1.1). Carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios continue to decline for ~ 2.5 Myr after OAE 2, until about the end of the Turonian, at which point they begin to increase again.

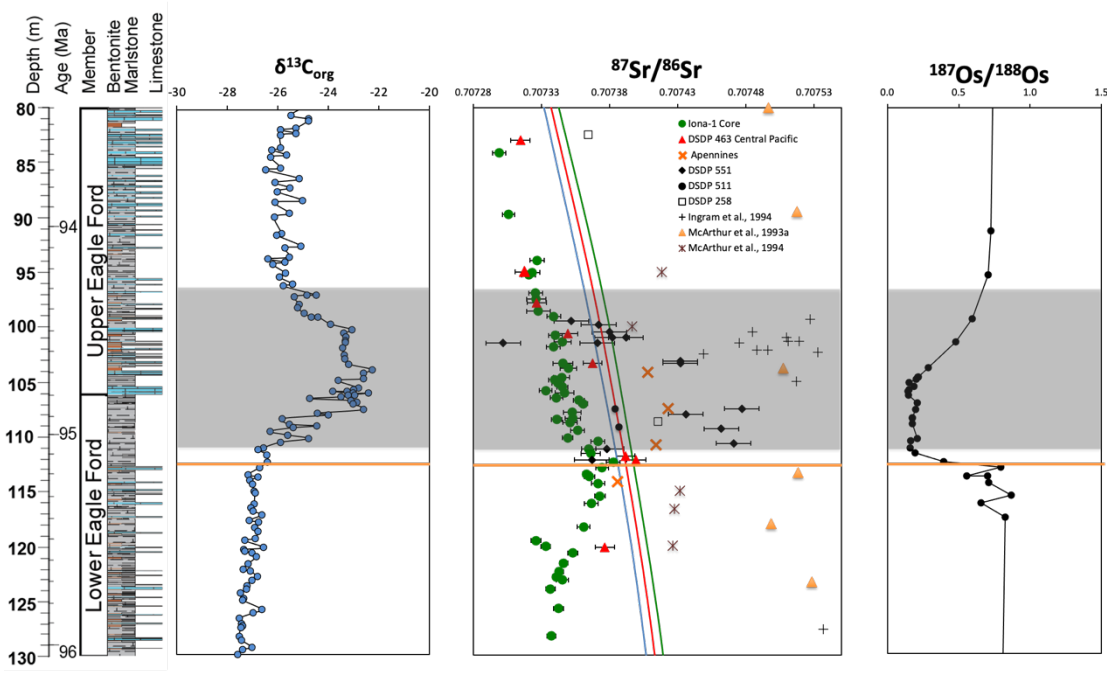


Figure 1.1: $\delta^{13}\text{C}_{\text{org}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for samples from the Iona-1 core.

The OAE 2 interval is shaded in gray, based on the shift to more positive $\delta^{13}\text{C}_{\text{org}}$ relative to background values (modified from Eldrett et al., 2014). Os isotope data are from Sullivan et al. (2020). Published $^{87}\text{Sr}/^{86}\text{Sr}$ data from other locales (McArthur et al., 1993b; 1994; Ingram et al., 1994; Bralower et al., 1997; Frijia and Parante 2008; Ando et al., 2009). The orange line indicates the onset of the shift to less unradiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Error bars represent $\pm 2\text{SE}$ uncertainty. The blue, red and green lines represent the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ minimum, mean and maximum values, respectively, of the LOWESS curve (McArthur et al., 2012).

Table 1.1: Measured $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios of the Iona-1 Core

Stratigraphic height (m)	Age	$^{87}\text{Sr} / ^{86}\text{Sr}$	2 s.e.
80.25	93.25	0.707299	4.90E-06
85.31	93.59	0.707306	4.46E-06
89.32	93.84	0.707327	5.11E-06
90.57	93.90	0.707323	5.59E-06
90.83	93.92	0.707321	5.07E-06
92.73	94.02	0.707326	5.07E-06
93.44	94.05	0.707326	6.90E-06
94.73	94.12	0.707328	8.80E-06
95.32	94.14	0.707339	5.02E-06
97.41	94.25	0.70734	4.95E-06
98.08	94.28	0.707346	6.28E-06
98.56	94.31	0.707339	5.19E-06
100.30	94.40	0.707346	7.43E-06
100.90	94.43	0.70735	5.94E-06
101.83	94.48	0.707345	5.80E-06
102.21	94.49	0.70734	4.50E-06
102.63	94.51	0.707342	4.44E-06
102.95	94.53	0.707345	4.08E-06
103.33	94.55	0.707333	4.76E-06
103.54	94.56	0.707347	6.85E-06
104.18	94.59	0.707341	4.56E-06
104.44	94.60	0.707357	4.04E-06
104.83	94.62	0.707361	3.18E-06
105.68	94.67	0.707353	6.46E-06
106.45	94.70	0.707353	5.69E-06
106.50	94.71	0.707341	3.88E-06
106.94	94.73	0.707351	5.28E-06
107.82	94.77	0.707356	5.09E-06
108.77	94.81	0.707349	3.85E-06
109.22	94.83	0.707371	4.97E-06

110.01	94.87	0.707365	5.14E-06
110.49	94.90	0.707366	7.09E-06
111.36	94.94	0.707383	5.11E-06
111.88	94.97	0.707375	4.47E-06
112.45	95.01	0.707363	3.03E-06
112.77	95.02	0.707365	3.96E-06
113.42	95.06	0.707372	4.90E-06
114.50	95.13	0.707373	3.75E-06
115.45	95.17	0.707367	5.09E-06
118.16	95.30	0.707361	4.57E-06
119.77	95.37	0.707326	3.66E-06
120.40	95.41	0.707333	3.45E-06
121.09	95.44	0.707353	3.51E-06
122.18	95.50	0.707346	3.01E-06
123.14	95.54	0.707343	2.91E-06
123.68	95.57	0.707341	2.89E-06
124.03	95.59	0.707345	4.45E-06
125.13	95.64	0.707337	3.42E-06
127.31	95.75	0.707342	3.65E-06
130.17	95.90	0.707337	3.14E-06
135.25	96.15	0.707362	6.09E-06

1.6 Discussion

Before interpreting the $^{87}\text{Sr}/^{86}\text{Sr}$ trend in the Iona core, it is important to consider the likelihood that it genuinely reflects secular change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2, rather than stratigraphic changes in diagenetic or local Sr cycling effects.

1.6.1 Diagenetic effects

Seawater derived Sr can be difficult to extract from mixed carbonate/siliciclastic lithologies without also releasing Sr from the detrital silicates. The ion exchange wash and weak acetic acid dissolution used in this study appears to have successfully targeted the release of Sr from carbonate minerals, based on the low Al concentrations in the acid leachates. A more difficult problem is the diagenetic transfer of silicate derived Sr into new carbonate mineral growth. However, there are a number of factors to consider that make recrystallization of the carbonates in the Iona core potentially less of a problem than in carbonate sediments from other settings. Firstly, the source of the carbonate mud is pelagic calcifiers (i.e. foraminifera and coccolithophores) that produce low magnesium calcite (LMC), which is the most diagenetically stable calcium carbonate polymorph. Secondly, the sediments have low permeability, and the observed carbonate cements have been interpreted to have precipitated in close diagenetic system (Eldrett et al., 2015b., Minisini et al. 2018). Accordingly, any cements that formed would likely re- incorporate seawater-derived Sr released to the pore fluids. Oxygen isotopes in the Iona-1 core show no obvious evidence for recrystallization of carbonates, such as low $\delta^{18}\text{O}$ values indicative of higher temperatures encountered during deep burial, or meteoric waters (Eldrett et al., 2015b). The bulk carbonate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in the Iona-1 core are similar to well preserved

calcite tests of calcite foraminifera reported in other locations of the WIS (Eldrett et al., 2015b and references therein). Hence, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the carbonate fractions were likely not altered by diagenetic processes. Hence it is concluded that the $^{87}\text{Sr}/^{86}\text{Sr}$ in the carbonate fractions measured here were unlikely to be reset by post-depositional diagenetic processes.

1.6.2 Local Sr cycling effects

Even in cases where diagenetic effects are negligible and the sample dissolution procedure only releases seawater-derived Sr from the samples, marine carbonates deposited in epeiric seas may record $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are different from the global ocean due to circulation restrictions and local Sr cycling. The study setting is located at the southern gateway to the WIS—an epeiric seaway that did not support a typical mid-Cretaceous marine fauna (McArthur et al., 1994, Eldrett et al., 2017, Minisini et al., 2018). Moreover, the WIS experienced climate oscillations that affected precipitation and freshwater inputs from rivers. These changes, in turn, affected salinity patterns, water column stratification and mixing in the Seaway, while longer term changes in sea level could ease or restrict the flow of water over the sill at the southern and northern gateways (Holmden et al., 1997a, 1997b; Cockran et al., 2003). The long length of the Seaway, equivalent to the distance between the present-day Arctic and Gulf of Mexico, increases the likelihood that local Sr cycling effects could be important in different parts of the Seaway at different times. The Late Cenomanian eustatic sea-level rise, and the location of the study setting near the southern gateway to the WIS lend support to improved circulation in the southern part of the Seaway during OAE 2. As an additional consideration, the large

difference in the Sr concentration between seawater and river waters dictates that the salinity must typically decrease to below ~15‰ before the local $^{87}\text{Sr}/^{86}\text{Sr}$ of brackish seawater can begin to deviate significantly from the global ocean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Anderson et al., 1992; Holmden et al., 1997a, 1997b; Holmden and Hudson, 2003). However, some forms of submarine groundwater discharge (SGD) have the potential to change seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios without any appreciable adjustments of salinity (Beck et al., 2013). A large Sr flux from SGD was likely important in the Late Cretaceous WIS in South Dakota (Cochran et al., 2003).

The role of local Sr cycling effects in the Seaway setting of the Iona-1 core is best evaluated with records from nearby locales in the WIS where circulation restriction is more likely—but these records do not exist. With spatially distributed records, a gradient in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, if present, could be used to reveal locations affected by local Sr cycling and the direction of change in local seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared the open ocean ratio. Until more local/regional records are available, the only remaining option is to compare the Iona-1 record to other published records regardless of their location. To do so, the records presented here were re-normalized to the SRM 987 ratio of 0.710251 obtained in this study (Figs. 1.1 and 1.2).

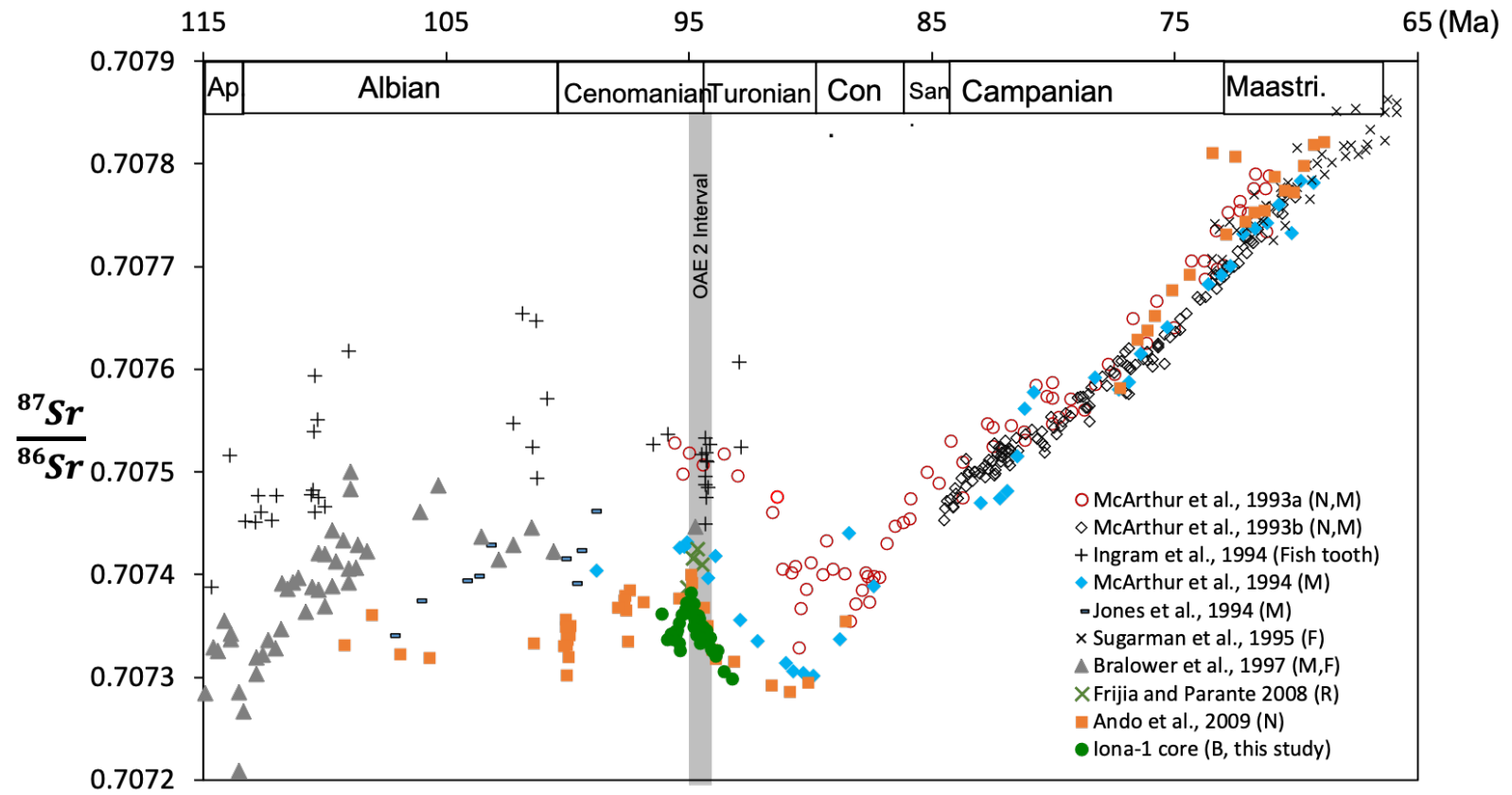


Figure 1.2: Compilation of Late Cretaceous $^{87}\text{Sr}/^{86}\text{Sr}$ data against time (GTS Gradstein et al., 2012) showing the landscape of changing $^{87}\text{Sr}/^{86}\text{Sr}$ over time (modified from Ando et al., 2009). All $^{87}\text{Sr}/^{86}\text{Sr}$ data have been recalibrated to SRM 987 0.710251 (this study). Data from other sources are fitted to the new timescale by simply updating the originally proposed numerical ages for the stage boundaries reported in age model of the paper. F = foraminifera; M = macrofossil; N = nannofossil chalk; R = rudists, B = bulk carbonate

All but one of the published $^{87}\text{Sr}/^{86}\text{Sr}$ records are inconsistent with the record of the Iona-1 core presented in this study. They are also inconsistent with each other (Fig. 1.1). Most of the published records depict higher inferred seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during OAE 2. The Iona-1 core record gives lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the LOWESS curve of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ (McArthur et al., 2012). Well-preserved rudists collected from near shore deposits representing shallow water settings in the Southern Apennines during OAE 2 (Frijia and Parante, 2008) gave even higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the LOWESS curve. These results were interpreted to reflect Sr inputs from local rivers, implying brackish waters and salinity stratification in this setting (Frijia and Parante, 2008). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios spanning OAE 2 are also high in several Deep Sea Drilling Project Sites (DSDP) Site 511 (Falkland Plateau South Atlantic; Bralower et al., 1997), DSDP Site 258 (Naturaliste Plateau, Indian Ocean; Bralower et al., 1997), DSDP Site 551 (Goban Spur, North Atlantic; Bralower et al., 1997), and the ODP Site 763B (Exmouth Plateau, Indian Ocean; Bralower et al., 1997). The carbonates in these deposits are primarily planktonic foraminifera that appear to have been altered (cf. Bralower et al., 1997). Although the data are sparse, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Site 511 overlap those from the Iona-1 core immediately before OAE 2, but then shift to relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the early stages of OAE 2 before decreasing again in the latter stages. The English Chalk (McArthur et al., 1993a) has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios before OAE 2 of any of the published records and a decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2 that is broadly consistent with the Iona-1 core record offset to higher ratios.

The $^{87}\text{Sr}/^{86}\text{Sr}$ record of OAE 2 that best matches the Iona-1 core is from DSDP Site 463, a carbonate succession draping the margin of a mid-Pacific atoll (Ando et al. 2009).

Although the DSDP Site 463 data are sparse in the OAE 2 interval, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are consistently lower than the other published records. Like the Iona-1 core and English Chalk, carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase before OAE 2 and decrease after the onset of OAE 2. However, the low sampling resolution of the DSDP Site 463 record does not permit a confirmation of the 150 kyr interval of no change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in the middle of OAE 2 that is present in the Iona-1 core record. To reconcile Site 463 with other published records, Ando et al. (2009) conceded that sections of the record could be shifted to lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios due to carbonate recrystallization in the presence of altered pore waters generated by water-rock interactions with basaltic volcanic rocks located at the base of the carbonate succession. The implications being that Sr bearing fluids may have migrated upwards through the sediment as a result of compaction and/or heating from below (Richter and Liang, 1993). However, the similarly low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios found in the Iona-1 core in the WIS, which is not underlain by basaltic volcanic rocks, indicate that these interactions were either inconsequential or did not happen at Site 463. Neither does it seem likely that Sr released into pore fluids from altered volcanic ash beds is responsible for lowering the carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Iona-1 core, as it would have to then be concluded that the similarities between the two records are a coincidence.

In summary, local Sr cycling effects could be responsible for the poor reproducibility observed in some shallow water carbonate records of changing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during OAE 2 (cf. Frijia and Parante 2008). Local Sr cycling effects, can be mistaken for alteration effects. Other $^{87}\text{Sr}/^{86}\text{Sr}$ records may have been altered during diagenetic (McArthur et al., 1993a; Bralower et al., 1997). Contamination of seawater derived Sr from lithogenic Sr released from detrital silicates has been recognized as problem hampering

accurate reconstructions of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios using bulk carbonate sediments for a long time, which is why carbonate fossils have been used instead (e.g., Veizer, 1983; Montanez et al., 1996; Young et al., 2009; Edwards et al., 2015; El Meknassi et al., 2018). If investigated in a systematic way in future studies, local Sr cycling effects can provide important information on circulation patterns and the general hydrography of epeiric seas like the WIS during OAE 2. At present, the reliability of the promising similarities between the $^{87}\text{Sr}/^{86}\text{Sr}$ records of the Iona-1 core and DSDP Site 463 core to gauge the likelihood that the more detailed record of the Iona-1 core accurately records changes in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the oceans during OAE 2.

1.6.3 Key patterns of change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2

LIP eruptions have been implicated to cause decreases to lower seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Cretaceous, including OAE 2 (Ingram et al., 1994; Jones and Jenkyns, 2001), but this is the first time that a decrease in carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios has been shown to occur synchronously with the decrease in seawater initial $^{187}\text{Os}/^{188}\text{Os}$ ratios. This suggests a casual effect where the hydrothermal weathering of the LIP basalts delivered large quantities of Sr to the oceans, beginning *ca.* 60 kyr before the onset of OAE 2 (Fig. 1.1). Continental weathering is assumed to have also increased the flux of Sr to the oceans during OAE 2, but its effect on the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is likely to be masked, in much the same way as Os isotopes, by the stronger change in Sr inputs from submarine volcanism. However, when the Os isotopes begin to shift back to baseline, indicating waning of submarine volcanism, the continental weathering flux of Sr may become visible again in the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ record. The stratigraphic interval of arrested change in the carbonate

$^{87}\text{Sr}/^{86}\text{Sr}$ record may signal the timing of this effect. These nuances in the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ record are used to estimate the sizes of the continental and hydrothermal input Sr-flux changes to the oceans during OAE 2 using an ocean Sr box model.

A unique solution for any change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is difficult to determine. For example, an increase in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ can be produced by: (1) increasing the continental weathering Sr flux, (2) decreasing the hydrothermal Sr flux, or (3) increasing the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the continental weathering flux. Accordingly, there are multiple ways to produce every change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ and they are not mutually exclusive. Accordingly, a conceptual model with additional geological constraints is needed to implement the box model. For example, an invariant hydrothermal flux during OAE 2 is not in accordance with the evidence for submarine volcanism during the event and can therefore be ruled out (Turgeon and Creaser 2008; Jenkyns, 2010; DuVivier et al., 2014; Sullivan et al., 2020). Reducing the continental weathering flux of Sr can generate the declining trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during OAE 2, but this is inconsistent with global warming predicted from volcanic outgassing of carbon dioxide, which should have accelerated continental weathering (Snow et al., 2005; Jenkyns, 2010). The Sr flux input from hydrothermal and continental weathering likely both increased in the early stages of OAE 2, as discussed above, but the hydrothermal inputs must have increased more to produce the early declining trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. It is reasoned that any further changes in the apportioning of the Sr flux inputs in the midst of OAE 2 should also lead to changes in the slope of the $^{87}\text{Sr}/^{86}\text{Sr}$ trend with time, if the relative flux change in one input is not overwhelmed by the relative flux change in the other.

As indicated above, there are two subtle changes of slope in the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ trend with time that occur in the midst of OAE 2 that may signal the first time since the onset of OAE 2, that the continental weathering Sr flux change is not completely dominated by the hydrothermal Sr flux. The first inflection point occurs in the midst of OAE 2 at the stratigraphic level (105 m depth) where massive volcanism ends or dramatically declines, as indicated by the rise in $^{187}\text{Os}/^{186}\text{Os}$ ratios (Fig. 1.1). Above this level the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater steadily increases, favoring a shift to greater relative inputs of Os from continental weathering. The second, stratigraphically higher inflection point occurs at 100 m depth in the core, coincident with the termination or dramatic decrease of organic carbon burial in ocean sediments, as signaled by the start of the return to pre-excursion $\delta^{13}\text{C}_{\text{org}}$ values at 100 m depth in the core. As increased organic carbon burial in the oceans during OAE 2 is at least partly tied to increased continental weathering inputs of nutrients needed to fuel additional productivity, the decline in $\delta^{13}\text{C}_{\text{org}}$ values at the end of OAE 2 is a logical place to expect continental flux perturbation.

Two additional constraints underpin the modeling. Firstly, after the continental weathering Sr flux perturbation terminates at 100 m depth in the core, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater must continue to steadily decline for another 1 million year (Fig. 1.1). The second constraint relates to the rising trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2, between 124 and 114 m depth in the core. This represents ~ 500 kyr of time before the LIP eruptions drove seawater $^{87}\text{Sr}/^{86}\text{Sr}$ in the opposite direction. Whether the rising trend before the LIP eruptions was due to increased continental weathering inputs, decreased hydrothermal inputs, or some combination of the two cannot be uniquely determined. And yet the choice made here affects the outcome of the forward modeling, specifically the relative

magnitudes of the modeled Sr flux increases from continental weathering and hydrothermal venting during OAE 2. For example, if the trend of increasing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 reflects increased continental weathering inputs of Sr to the oceans, then a larger increase in hydrothermal Sr inputs is needed to match the decreasing trend at the onset of LIP volcanism, as there is no reason to reduce the continental Sr weathering flux at this time, as it too would be expected to increase. By contrast, a larger relative increase in continental weathering is required at the onset of the LIP volcanism in the case where the increasing trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 reflects decreasing hydrothermal inputs of Sr to the oceans. As it is not known which scenario is correct, two forward models of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ changes during OAE 2 are produced, resulting in two estimates of the change in the continental weathering input of Sr to the oceans during OAE 2.

1.6.4 Estimating Sr flux perturbations to the oceans during OAE 2

A box model is used to quantify the perturbations of the ocean Sr cycle that can account for the observed changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during OAE 2. A coupled Sr mass and Sr-isotope mass balance approach is used here. Parameters are based on modern values, adjusted for the Cretaceous based on available constraints that are described in detail below.

The time dependent change in the inventory of Sr in the oceans is represented by Eq. 1,

$$\frac{dN_{\text{Sr}}}{dt} = J_{\text{riv}} + J_{\text{H}} + J_{\text{dia}} - J_{\text{ppt}} \quad (1)$$

where N_{Sr} represents moles of Sr in the oceans and J_{riv} , J_H , J_{dia} and J_{ppt} are the riverine (i.e. continental weathering), hydrothermal, diagenetic and carbonate precipitation fluxes, respectively. The corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the seawater is given by Eq. 2,

$$\frac{dR_{SW}^{Sr}}{dt} = \frac{J_{riv}^{Sr}(R_{riv}^{Sr} - R_{SW}^{Sr}) + J_H^{Sr}(R_H^{Sr} - R_{SW}^{Sr}) + J_{Dia}^{Sr}(R_{Dia}^{Sr} - R_{SW}^{Sr})}{N_{Sr}} \quad (2)$$

where R_{SW}^{Sr} represents the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ocean Sr reservoir and R_{riv}^{Sr} , R_H^{Sr} , and R_{Dia}^{Sr} are the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the riverine, hydrothermal, and diagenetic Sr inputs, respectively.

Initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr input fluxes were obtained from present-day estimates (Table 1.2) with several adjustments that are explained below. The output flux of Sr depends on the N_{Sr} and is parameterized using a first-order rate constant calculated from the initial conditions. As with many box models, steady state is assumed prior to running the model.

Table 1.2: Comparison of modern ocean Sr budgets with inferred boundary conditions for the OAE 2 models

Modern ocean Sr budget							Late Cretaceous ⁸ Ocean Sr budget				
	min	Sr	max	min	⁸⁷ Sr/ ⁸⁶ Sr	max	ref.	change ⁷	Sr	⁸⁷ Sr/ ⁸⁶ Sr	ref.
Reservoir	moles								moles		
Seawater Sr		1.25E+17			0.70918		2		1.25E+17	0.70733	1
Sr residence time (Myr)		1.48							1.35		
					value or						
Sr Fluxes	10 ⁹ mol/y				weighted avg.				10 ⁹ mol/y		
global rivers		47.6			0.71107		3				
SGD 7		17.5	28		0.7089		3				
global rivers 54.6		65.1	75.6		0.71049						
riverine volcanic ash dissolution		1			0.705		3				
eolian volcanic 0.0114		0.017	0.0228		0.705		3				
all continent 55.6		66.1	76.6		0.71040				66.1	0.70791	
diagenetic		5.5			0.70849		3		5.5	0.70733	
all non hydro 61.1		71.6	82.1		0.71026		3		71.6	0.70786	1
hydrothermal Sr inputs ¹		12.7		0.7025	0.7031	0.7037	3	1.65	20.9	0.7055	4,5
carbonate precipitation output		84.3					1		92.5		1

1. this study; measured or calculated from mass balance

2. Richter et al., (1992)

3. Peucker-Ehrenbrink and Fiske (2019)

4. Bickle and Teagle, (1992), Kawahata et al., (2001)

5. Antonelli et al., (2017)

6. Coogan and Dosso (2012)

7. 1.65 times increased sea floor spreading rate; Berner, 1994; 3.8 times increased Sr concentration in the middle Cretaceous oceans (cf. Antonelli et al., 2017)

8. Bolded values are used in the model simulations of this paper.

Two revisions were made to the modern ocean Sr budget to account for differences in the Late Cretaceous Sr cycle. First, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of all continental sources of Sr (the riverine flux, submarine groundwater discharge, and terrestrial volcanic sources are combined into the J_{riv}) was adjusted from the present-day ratio of 0.71040 down to 0.70791 in order to achieve a steady-state $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Late Cretaceous seawater representing a period of unchanging $^{87}\text{Sr}/^{86}\text{Sr}$ ratios at the base of the study core (Fig. 1.1). This is not meant to imply that the ocean Sr cycle was truly in steady state at this time, but rather, to give a set of initial conditions against which changes in ocean Sr cycling that occur above this level in the core can be compared to. Second, the background hydrothermal flux was increased by 65% in accordance with reconstructions of higher Cretaceous seafloor spreading rates compared to the modern (Berner 1994). It is assumed that Late Cretaceous N_{Sr} was comparable to the modern reservoir of size of 1.25×10^{17} moles of Sr, which gives a residence time of 1.35 Myr (Table 1.2). Multiple lines of evidence suggest that the Sr concentration of seawater was higher in the Late Cretaceous than today (Steuber and Veizer, 2002; Coogan 2009; Antonelli et al., 2017; Akhtar et al., 2020; Zhang and DePaolo, 2020) and consequently, the oceanic Sr residence time was longer than today. To investigate the sensitivity of the model results to higher seawater Sr concentration, the model is run for various Sr reservoir size up to 5-times larger than modern, which corresponds to a residence time >5 Myr.

The ocean Sr cycle is forced by changing one or both of the two largest input Sr fluxes to the oceans, J_{riv} and J_H . A step-change in either flux causes an initially relatively quick change in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater that slows exponentially with time as it

approaches the steady state $^{87}\text{Sr}/^{86}\text{Sr}$ ratio within five residence times (~ 7 Myr). Because OAE 2 lasts for maximum of ~ 800 Kyr, none of the flux perturbations employed to simulate the trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio during OAE 2 occurs long enough for the ocean Sr cycle to reach steady state.

The simulations show that the continental weathering flux of Sr to the oceans increased by 1.8–1.85-times the value of the modern Sr flux of 66.1×10^9 moles/y (Table 1.2), depending on how the rising trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is treated before OAE 2 is treated as discussed in Section 6.3 (Fig. 1.3). The lower estimate is the result of treating the increasing trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 as the effect of increasing continental weathering inputs of Sr to the oceans and constant hydrothermal inputs. The higher estimate treats the increasing trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 as the effect of decreasing hydrothermal fluxes of Sr to the oceans and constant continental weathering inputs. These model results only consider changes in the input fluxes of Sr to the oceans and make the assumption that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the continental weathering flux was constant. Considering that OAE 2 occurred near the peak of the Late Cenomanian transgression, if the flux-weighted average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the continental weathering flux changed during OAE 2, it would have likely increased due to the drowning of carbonate platforms with low $^{87}\text{Sr}/^{86}\text{S}$ ratios. If this is correct, then the increase in the continental weathering flux of Sr to the oceans would have been lower than the results shown in Fig. 1.3.

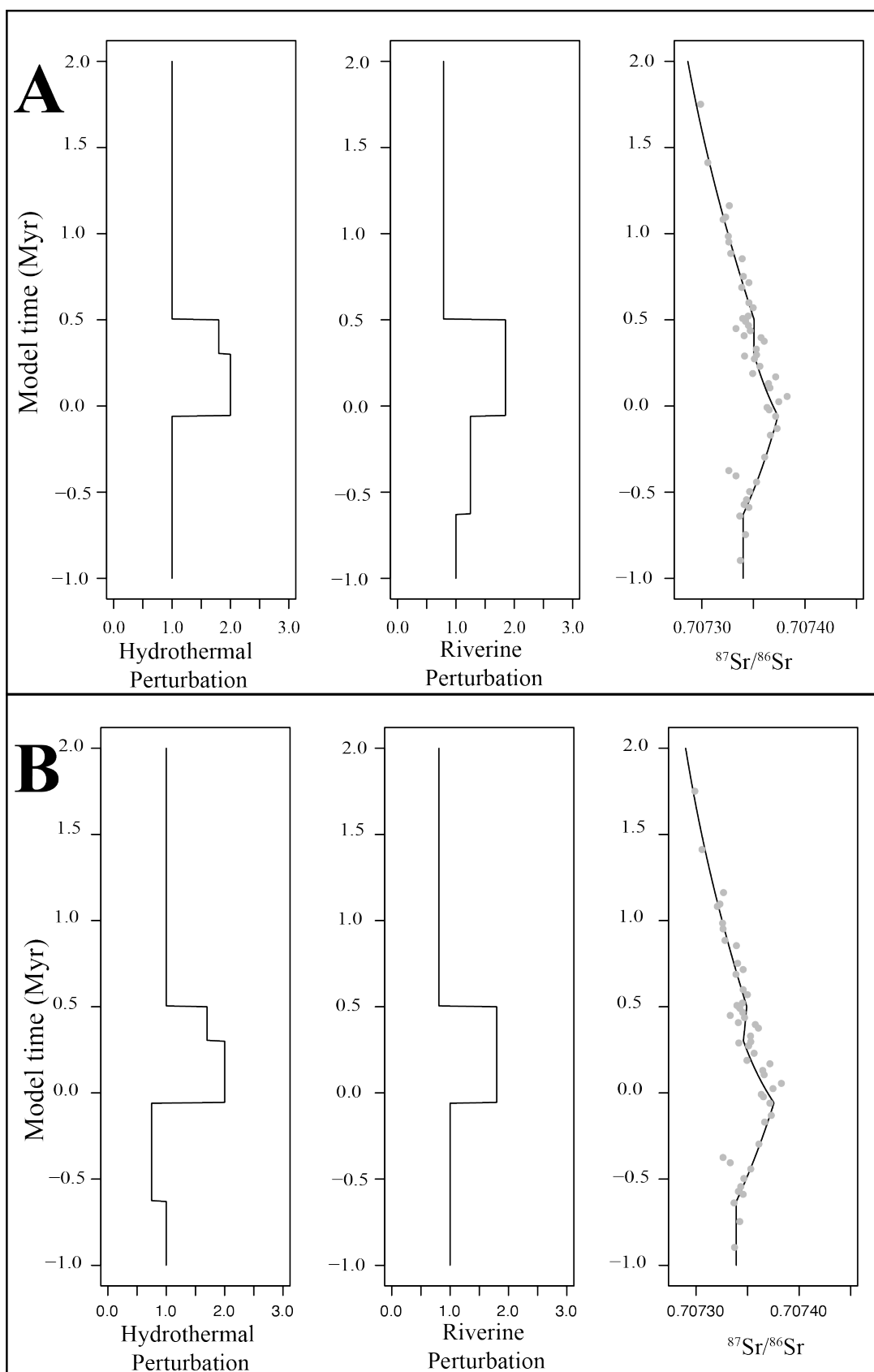


Figure 1.3: Box model results of the seawater strontium isotope ratio when the hydrothermal and riverine fluxes are changed simultaneously. These scenarios were generated to best fits to the Iona-1 $^{87}\text{Sr}/^{86}\text{Sr}$ data, including the mid-OAE 2 150kyr stasis in $^{87}\text{Sr}/^{86}\text{Sr}$. The perturbation changes are normalized to pre-perturbation fluxes (Table 1.2). Onset of OAE 2 is at model time Rather than an abrupt drop in hydrothermal or riverine flux to post OAE 2 values, there is a sequential drop in both the hydrothermal and riverine guided by the Os isotope relaxation and plateau in C isotopes (Fig. 1.1). A.) In this scenario, the hydrothermal flux is increased by 100%, relative to the perturbation baseline as suggested by the increase in osmium isotopes. The continental weathering flux is increased by 25% prior OAE 2, followed by an additional 48% increase during OAE 2 (1.25x to 1.85x the pre perturbation baseline). The continental weathering flux is then decreased sequentially to generate the pause and the decrease in $^{87}\text{Sr}/^{86}\text{Sr}$. B) A similar pattern is produced by decreasing the hydrothermal flux by 25% and keeping the riverine flux constant leading up to OAE 2. The hydrothermal flux is increased by 162% increase during OAE 2 before returning to baseline after the return in Os isotopes. The continental weathering flux is increased by 1.8x the pre-perturbation baseline during OAE 2.

By considering the sensitivity of the model results to differences in initial conditions, it is unlikely that the continental weathering flux of Sr to the oceans during OAE 2 is underestimated. Moreover, assuming that the increase in continental Sr flux scales proportionately to the continental Ca, Li and nutrient fluxes, the much smaller continental weathering response to the LIP eruption suggested here—compared to previous estimates of a threefold increase (Blättler et al., 2011; Pogge on Strandmann et al., 2013)—has important implications for the ocean eutrophication model of OAE 2, where the expansion of ocean anoxia and increased burial of organic carbon is largely driven by increased productivity that is stimulated by increased continental weathering supplies of nutrient phosphate to the oceans (see below). The lower continental weathering response elevates the importance of other contributing factors to anoxia, such as the role played by reduced metals and gases to the oceans from the LIP eruptions (Sinton and Duncan, 1997), the paleogeography and circulation of the proto-North Atlantic nutrient trap and its surrounding epeiric seas (Trabucho-Alexandre et al., 2010), positive feedbacks related to P-recycling efficiency (Ingall and Jahnke, 1994), and more organic carbon burial due less efficient remineralization in anoxic bottom waters (increased preservation).

The Iona-1 record shows decreasing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios continuing after the cessation of OAE 2. Because the forcing from excess Sr input from LIP volcanism was removed in the early middle part of OAE 2, and the continental weathering flux perturbation was removed near the end of OAE 2, the expectation is that seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater should eventually reverse and reach a new higher steady-state $^{87}\text{Sr}/^{86}\text{Sr}$ ratio after about five residence time. Instead, it continues falling with no evidence of change at the end of OAE 2. This pattern can be modeled to produce a new steady state by

decreasing the hydrothermal input Sr flux to the oceans at the end of the peak interval of the CIE or by decreasing the continental weathering Sr flux. The latter is favored here, because excess hydrothermal inputs of Sr to the oceans is expected to end in concert with the relaxation of initial $^{187}\text{Os}/^{186}\text{Os}$. One other possibility is that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of continental weathering decreased around this time. This would require large changes in the types of continental rocks exposed to weathering, which is unlikely on short time scales. It is even less likely that the hydrothermal Sr flux would change without first signaling a change in seawater initial $^{187}\text{Os}/^{186}\text{Os}$, so a reduction in the continental weathering input is the favored explanation.

Published records show that the declining trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ continued for 2.5 Myr until about the end of the Turonian (Fig. 1.2). Thereafter, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios rise steeply for the next ~25 Myr, consistent with a first order decrease in ridge-crest hydrothermal activity in the oceans (Berner, 1994). The increasing trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is the dominant trend over the Late Cretaceous period, which continues into the Cenozoic (Vérard et al., 2015). It is therefore the intervals of decreasing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ that are anomalous when considering the broader time frame (Jones and Jenkyns, 2001). This is evidence that continental weathering Sr flux inputs were either much smaller in the Late Cretaceous than they are today, or that hydrothermal Sr flux inputs were much larger (Ingram et al., 1994). These broader findings are mirrored in this more detailed study of ocean Sr cycle changes during OAE 2.

1.6.5. Additional considerations regarding ocean eutrophication and residence time

The ocean eutrophication model (Schlanger and Jenkyns 1976; Demaison and Moore, 1980; Pedersen and Calvert, 1990) predates the broader understanding of OAE 2 that has emerged in recent years. Most notably, it has been established that eruptions of one or more LIPs triggered the event (Turgeon and Creaser, 2008; DuVivier et al., 2014; Sullivan et al., 2020), that the small and relatively secluded proto-North Atlantic Ocean functioned as nutrient trap (Trabucho-Alexandre et al., 2010), that records of environmental changes during OAE 2 from the proto-North Atlantic ocean and surrounding seas may give a distorted picture of the global change impacts, and that the Caribbean LIP erupted near the main oceanic gateway to the proto-North Atlantic in Central Americas (Fig. 1.1). The latter could expedite the delivery of: (1) trace metal nutrients to the proto-North Atlantic, most notably iron, which limits primary productivity even in nutrient replete regions of the modern oceans (Leckie et al., 2002; Monteiro et al., 2012), and (2) anoxic, intermediate depth waters to the proto-North Atlantic that could increase the preservation of exported organic matter from the photic zone and its burial in the proto-North Atlantic region, while over time increasing productivity and anoxia through the positive feedback involving sedimentary phosphorous recycling (Ingall et al., 1993). In other words, the eruption of Caribbean LIP would have increased organic carbon burial in the proto-North Atlantic basin without any increase in continental weathering rates during OAE 2. Additional considerations are needed to explain the geographic variability and magnitude of the OAE 2 C isotope excursion, which cannot simply be attributed organic carbon burial (Owens et al., 2018).

The modeled excess of hydrothermally sourced Sr to the oceans can be converted to implied volumes of new oceanic crust produced by the LIP eruption(s) that triggered OAE 2. For this, the modern estimated ridge-crest hydrothermal Sr exchange flux of 6×10^8 mol of strontium per cubic km of new crust is used (Ingram et al., 1994) and assume that this is broadly applicable to hydrothermal Sr exchange between seawater and LIPs (Table 1.3). A doubling of the hydrothermal Sr flux at the onset of OAE 2 (the forcing that is needed to match the $^{87}\text{Sr}/^{86}\text{Sr}$ data in Fig. 1.3A) would add 39.9 km^3 of additional new crust production per year on a global scale. Considering the duration of the model perturbation in the hydrothermal Sr flux of 450 kyr, this equates to 15.7 million km^3 of extra basalt production over the duration of OAE 2. The volume of basalts erupted by the Caribbean LIP was estimated by Larson (1991) to be 20.41 million cubic kilometers, indicating that there is enough basalt in the Caribbean LIP to account for the increase in hydrothermal Sr inputs. It seems unlikely that most of the Caribbean LIP (nearly 80%) would have erupted in this relatively short time frame. Larson (1991) documented other LIPs with similar eruption ages that could have also contributed hydrothermal Sr to the oceans, thus increasing the total volume of plateau basalt volcanism to 58.2 million cubic kilometers. Only 27% of this larger volume of LIP basalt would need to erupt in the estimated time frame of 450 kyr.

Table 1.3: Calculated volume of oceanic plateau basalt equivalent from the hydrothermal flux during OAE 2

				Doubling the hydrothermal flux			100% eruption of Carrebean LIP		
Modern Sr				Sr Fluxes	10 ⁹ mol/y	⁸⁷ Sr/ ⁸⁶ Sr	Sr Fluxes	10 ⁹ mol/y	⁸⁷ Sr/ ⁸⁶ Sr
	10 ⁹ mol/y	ref.	change ³						
Continental	66.01	1		Continental	66.01	0.7079	Continental	66.01	0.7079
Hydrothermal	12.70	1	1.65	Hydrothermal	20.96	0.7055	Hydrothermal	20.96	0.7055
				Fraction of total input			Fraction of total input		
Ocean crust production rate (mol/Km ³)				Continental	0.76		Continental	0.76	
	6.00E+08	2		Hydrothermal	0.24		Hydrothermal	0.24	
				Onset of OAE2 ⁴ mol/y			Onset of OAE2 ⁴ mol/y		
Estimated Volume of Carrebean LIP	Km ³			Hydrothermal	4.19E+10		Hydrothermal	4.82E+10	
	2.04E+07	5		Crust Production Km ³			Crust Production Km ³		
				Background	34.93		Background	34.93	
				Background+LIP	69.85		Background+LIP	80.28	
				LIP	34.93		LIP	45.36	
				Production over OAE2			Production over OAE2		
				1.57E+07			2.04E+07		
				0.77			1.00		
				Fraction of CLIP			Fraction of CLIP		

1. Peucker-Ehrenbrink and Fiske (2019)

2. Ingram et al., (1994)

3. 1.65 times increased sea floor spreading rate; Berner, 1994

4. Values used in the model simulations of this paper.

5. Larson 1991

This calculation can provide insight into the likely residence time of Sr in the oceans during the Late Cretaceous and by extension, the Sr concentration of seawater. At higher residence times, a larger perturbation of the hydrothermal Sr flux, and therefore an unreasonably large volume of basalt, would be needed to effect significant changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$. This is illustrated by a sensitivity test of varying Sr reservoir sizes (Fig. 1.4) with the Late Cretaceous boundary conditions described in Table 1.2. For simplicity, the model is forced by an increase in continental weathering of Sr leading up to and during OAE 2, combined with the emplacement of 100% of the estimated volume of the Caribbean LIP erupted over the duration of OAE 2 (Table 1.3). As shown in Figure 4, as the ocean Sr reservoir size progressively increases, the modeled changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ become smaller, and it becomes increasingly difficult to match the magnitude of the observed decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2 in the Iona-1 core. Accordingly, at the higher residence times considered in Fig. 1.4, a larger hydrothermal forcing—and by extension, a volume of basalt greater than the Caribbean LIP—would be required, representing an untenable scenario. In sum, this back-of-the envelope calculation indicates that despite estimates for higher Sr concentrations of Late Cretaceous oceans relative to the modern, which in some calculations are significantly larger by a factor of four to five (e.g., Renard, 1989; Wallmann, 2001; Steuber and Veizer, 2002; Holmden and Hudson, 2003; Coggon et al., 2010; Antonelli et al., 2017), the maximum reasonable Sr residence time is likely to not have been dramatically different.

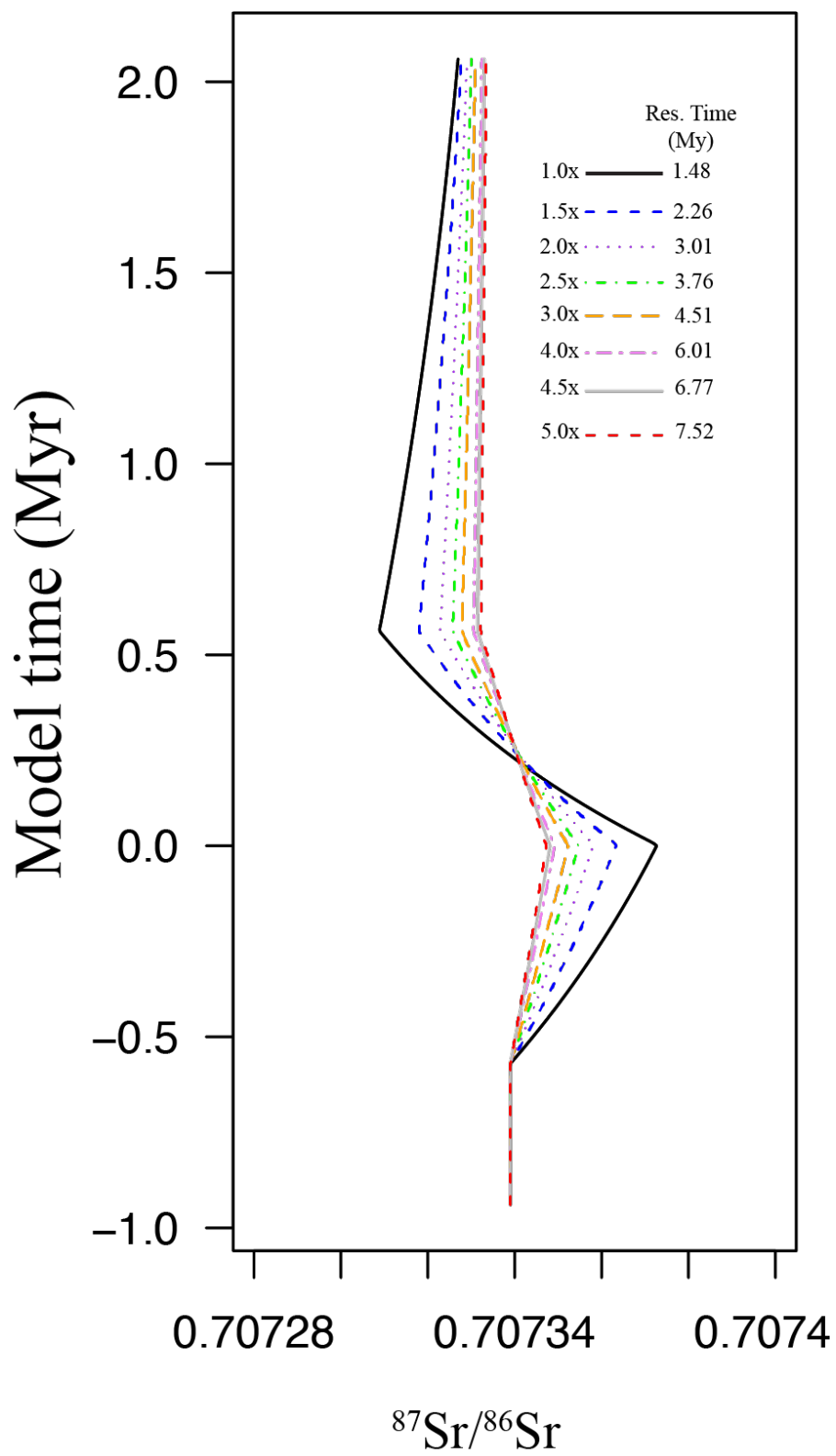


Figure 1.4: Sensitivity of the box model to the marine residence time of Sr. The residence times reflect increasing the Sr reservoir size relative to the Late Cretaceous boundary conditions (Table 1.2) up to a residence time of about 7.52 Myr, five times longer than the baseline. The model is forced by increasing continental fluxes (Table 1.3) and an increase in hydrothermal flux during OAE 2 that is equivalent to the entirety of the Caribbean LIP being emplaced over OAE 2. As the residence time increases, the difference in modeled $^{87}\text{Sr}/^{86}\text{Sr}$ over OAE 2 becomes progressively smaller. At high residence times, it is impossible to match the decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ without invoking unreasonable basalt eruption or considering other aspects of the Sr cycle. Onset of OAE 2 is at model time 0

The only way to maintain a high Sr concentration in seawater, and a reasonable oceanic residence time is to increase the throughput of Sr, i.e., inputs and outputs of Sr would both have to increase relative to the modern. This could include higher Sr flux inputs from carbonate sources of Sr, including weathering of exposed carbonate platforms in epicontinental marine settings, diagenetic fluxes of Sr from carbonate dissolution, and submarine groundwater discharge in carbonate platform settings (Chaudhuri and Clauer 1986; Huang et al., 2011; Beck et al., 2013; Peucker-Ehrenbrink and Fiske, 2019; Danish et al., 2020), analogous to a process suggested to influence the Ca isotope composition of seawater (Holmen et al., 2012). The main benefit of higher carbonate dissolution fluxes is that there is little effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater if the weathered carbonates are, geologically, recently deposited. A second benefit of carbonate weathering is that it introduces the alkalinity that is needed to increase the removal of Sr from the oceans through increased carbonate precipitation rate. Another source of Sr to the oceans that was likely more important in the Cretaceous than it is today, is the submarine weathering of exposed basalt along the flanks of the mid-ocean ridges (cf. Cogné and Humler 2006). As the temperature of ocean bottom waters were much warmer in the Cretaceous (14°C; Huber et al., 2002) than in present oceans (4°C), the submarine weathering flux of Sr to the oceans could have been, at its maximum, twice as high as the modern flux (Beck et al., 2013; Peucker-Ehrenbrink and Fiske, 2019). In contrast to the carbonate dissolution/weathering fluxes, which affect the Sr concentration of seawater more than its $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, low-temperature submarine weathering of basalt by warm bottom waters would drive seawater to higher Sr concentrations and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Holmden and Hudson 2003; Anthonelli et al., 2017).

The submarine weathering flux of Sr to the oceans prompts the consideration of additional, but related, assumptions that affects the impact of the validity of the calculations. The first one is that the box model, that is configured for this study, does not allow for any gain or loss of Sr during hydrothermal interactions between seawater and basalt. All Sr from seawater that enters the oceanic crust is exchanged, mole for mole, with basaltic Sr, which is then returned to seawater through venting. This is a common assumption that is made in most ocean Sr box models. Recently, Antonelli et al. (2017) demonstrated that secular changes in the Mg and Ca concentrations of seawater affects the Sr exchange capacity of the oceanic crust. For example, the low concentrations of Mg in Cretaceous seawater results in lower fluxes of basaltic derived Sr to the oceans by about 20%, which results in higher predicted $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the hydrothermal flux. To account for this effect, a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7055 was used in this paper, for the hydrothermal flux of Sr to oceans during OAE 2 (Bickle and Teagle, 1992; Kawahata et al., 2001) rather than the more conventional $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7025–to 0.7037. The latter range of ratios reflect the modern hydrothermal Sr flux, where all seawater Sr that circulated through the oceanic crust was exchanged for basaltic derived Sr due to the high present day Mg concentration of seawater.

While the data in this study support increased continental weathering inputs of Sr, Ca and nutrients to the oceans during OAE 2, the increase suggested by Sr isotopes is lower than the threefold increase suggested by Ca isotopes (Blättler et al., 2011), which was affected by methodological issues. The record and interpretation have since been revised by DuVivier et al. (2015). Another study using $\delta^7\text{Li}$ as a continental weathering proxy is seemingly in agreement with the original Ca isotope study (Pogge von Strandmann et

al., 2013). However, the origin of the negative Li isotope excursion upon which this estimate is based could have multiple interpretations. In fact, the decrease from 20–25‰ before OAE 2, to between 7–10‰ during OAE 2, overlaps $\delta^7\text{Li}$ values measured in high temperature hydrothermal fluids of 8‰ and in basalt from 5–7 ‰ (Sun et al., 2018). The authors, however, preferred a continental weathering source interpretation that related the change in Li isotopes in marine carbonates to the fractionation of Li isotopes during continental weathering in a period of enhanced (wet) hydrological cycle. In any case, the Li isotope effect is not a small one, and deserves to be followed up with additional study. In the meantime, climate and ocean circulation model studies are needed to examine the effects of the relatively smaller continental weathering flux increase of ~1.8-times found in this study.

1.7 Conclusions

A high-resolution record of change in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater during OAE 2 was reconstructed from the carbonate fraction of the Iona-1 core in the southern WIS. These new $^{87}\text{Sr}/^{86}\text{Sr}$ data fill in missing details for the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve over this time interval, resolving questions about the timing and magnitude of change in hydrothermal and continental weathering fluxes of Sr to the oceans during OAE 2. Although submarine eruptions of LIPs have been implicated in the decrease in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2, and other Cretaceous OAEs, for some time, this is the first time that the decrease $^{87}\text{Sr}/^{86}\text{Sr}$ is shown to have been synchronous with the decrease in the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater, which is the benchmark proxy for tracing massive volcanism during OAE 2. The declining trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ pauses in the middle of OAE 2 for

about 150kyr, which is interpreted to reflect the end of at this time, which allows effects of increased continental weathering fluxes of Sr to the oceans to become visible in the record of changing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ for the first time since onset of OAE 2. An ocean Sr box model was employed simulate the change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through OAE 2, and to quantify hydrothermal and continental weathering flux changes. The 1.8–1.85-times increase in the continental weathering flux during OEA 2 estimated using Sr isotopes in this study is smaller than threefold increase using Ca and Li isotopes as continental weathering proxies. This lower continental weathering rate has important ramifications for how OAE 2 and OAEs in general originate and evolve, and what controls nutrient delivery to the oceans during these events.

The modeling and overall conclusions, of this study also hinge on the assumption that the record of changing carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Iona-1 core accurately records changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ during OAE 2 and immediately before and after OAE 2 as well. The only way to test this assumption is to further examine the Sr record in other marine carbonate OAE 2 successions around the world at the same level of resolution. Finally, a forward model, such as the one employed in this study, helped to explore these relative changes but an inverse model could be used in future work to improve on the estimates presented here.

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CHAPTER 2: CHANGES IN THE INTENSITY OF LIP VOLCANISM TRACKED BY CR ISOTOPES DURING OCEAN ANOXIC EVENT 2

2.1 Abstract

Chromium is a redox-sensitive element with mass-dependent fractionations that reflect changes in its oxidation state. Chromium(VI) is the dominant oxidation state of Cr in the oceans where it forms the soluble chromate oxyanion. In biologically active regions of the oceans, Cr(VI) is susceptible to reduction to Cr(III) species, which are less soluble and, thus, prone to scavenging and removal by sinking particles. Reduction favors enrichment of the light Cr isotopes in Cr(III). Therefore, in settings where the produced Cr(III) is removed, the residual pool of Cr(VI) is shifted to higher $\delta^{53}\text{Cr}$ values. This allows for the possibility of using Cr isotopes as ocean paleo-redox proxy. Expanding ocean anoxia in the geological past should correlate with increased sedimentary $\delta^{53}\text{Cr}$ values in marine sediment. However, a test of this prediction, performed on a carbonate succession in the Cretaceous Western Interior Seaway (WIS) deposited during Ocean Anoxic Event 2 (OAE 2), finds that sedimentary $\delta^{53}\text{Cr}$ values decreased during the period of increased ocean anoxia rather than the expected increase. This finding was attributed to submarine eruptions of the Caribbean Large Igneous Province, the proposed trigger for OAE 2, which delivered large quantities of isotopically light Cr(III) and other trace metals to the oceans from hydrothermal weathering of basalt at the eruption site. This study presents a new high-resolution record of the redox proxies $\delta^{53}\text{Cr}$, Ce/Ce^* , and Eu/Eu^* , in carbonate fractions from shales deposited during OAE 2. The samples come from the Iona-1 core of the Eagle Ford Formation in the WIS. The $\delta^{53}\text{Cr}$ begins with a gradual increase from 127 to 115 m

before starting to decrease ~60 kyr before the onset of OAE 2. These changes are coupled with decreasing Ce/Ce* and Eu/Eu* that indicate mixing of LIP-derived hydrothermal fluid and resulting in changing local redox conditions in the WIS bottom waters. The carbonate $\delta^{53}\text{Cr}$ response lags behind that for Ce/Ce* and Eu/Eu* but begins to record the increase in LIP-derived hydrothermal source fluid in the waters ~250 kyr before the CIE. Overall, the redox-sensitive rare earth elements (REE) reinforce the conclusion that the carbonate $\delta^{53}\text{Cr}$ was responding to changes in hydrothermal activity that deposited isotopically light Cr(III) resulted in the negative observed excursion.

2.2 Introduction

The Cenomanian – Turonian Ocean Anoxic Event 2 (OAE 2) represents some of the largest biogeochemical perturbations of the global carbon cycle in the Phanerozoic (Schlanger and Jenkyns 1976). Although the stratigraphic expression of the event varies, the event is associated with global warming, increase nutrient delivery into the ocean, and spread of low oxygen and euxinic marine environment (see overview in Jenkyns 2010). Hence, understanding the development of Mesozoic OAEs is important for constraining the effects of modern anthropogenic warming conditions. The extreme warmth associated with OAE 2 was punctuated by a period of cooling, known as the Plenus Cold Event (Gale and Christensen, 1996; Forster et al., 2007; Jenkyns et al., 2017; O'Connor et al., 2020).

Studies on the onset of OAE 2 have concluded that OAE 2 was preceded by the emplacement of either the Caribbean Large Igneous Province (CLIP; Snow et al., 2005; Turgeon and Creaser, 2008; Du Vivier et al., 2014; Scaife et al., 2017) or the High Arctic

Large Igneous Province (Du Vivier et al., 2014; Kingsbury et al. 2018; Schröder-Adams et al., 2019; Sullivan et al. 2020). Associated with the increases in ocean basin hydrothermal activity is a ~1.8 times increase in continental weathering activity during OAE 2 estimated from $^{87}\text{Sr}/^{86}\text{Sr}$ (Nana Yobo et al., 2021). This volcanic activity likely released large quantities of CO_2 , hydrothermally sourced iron, and increased nutrient delivery into the ocean that thereby drove primary productivity (Tsikos et al., 2004; Jenkyns 2010). Since OAEs involve the widespread development of oxygen-deficient water masses, redox-sensitive isotope systems were potentially perturbed in the global ocean during these intervals. To better understand the changing redox condition, this study investigates the response of the development of anoxia and changing redox conditions in the ocean during OAE 2 using Cr isotopes. Samples studied from OAE 2 are from the Iona-1 core that was drilled on a carbonate shelf at the southern gateway to the Cretaceous Western Interior Seaway (WIS) in present-day southwest Texas. To better constrain changing redox conditions, the Cr isotope proxy is used here together with Ce/Ce^* and Eu/Eu^* to better understand the changing redox conditions of the ocean during OAE 2 as well as the effect of increased hydrothermal activity on the chromium response.

2.3 Chromium Isotope Fractionation and Anoxia

Chromium is a redox-sensitive metal with two dominant valence states and offers the ability to constrain the paleoredox state of the ocean. In the marine environment, Cr has two oxidation states, Cr(VI) oxyanion (CrO_4^{2-} or HCrO_4^-) and Cr(III)-compounds (Rai et al., 1989; Fendorf, 1995). Cr(VI) is soluble, while Cr(III) is particle reactive (Rai

et al., 1989). Chromium has four stable isotopes, ^{50}Cr , ^{52}Cr , ^{53}Cr , and ^{54}Cr , with abundances of 4.345%, 83.789%, 9.501%, and 2.365%, respectively. The measurements of $^{53}\text{Cr}/^{52}\text{Cr}$ isotope ratios are generally expressed in δ notation relative to the NIST SRM 979 (Shields et al., 1966), where

$$\delta^{53}\text{Cr}_{\text{sample}} [(^{53}\text{Cr}/^{52}\text{Cr})_{\text{sample}} / (^{53}\text{Cr}/^{52}\text{Cr})_{\text{SRM979}} - 1] \times 1000$$

Cr(III) is the abundant species in continental rocks, hence during oxidative weathering, Cr(III) can be oxidized to Cr(VI) through direct reaction with Mn-oxides (Eary and Rai 1987; Fendorf and Zasoski, 1992). The oxidized Cr(VI) is then transported by rivers into the oceans and becomes part of the Cr inventory. Within the ocean, Cr(VI) can be taken up by carbonates as has been demonstrated by laboratory experiments (Hua et al., 2007; Tang et al., 2007) or ultimately reduced to Cr(III) (Reinhard et al., 2014). The reduction can occur through a series of pathways, in the presence of an organic compound, reduced Fe species, hydrogen sulfide, aerobic and anaerobic bacteria (e. g. Døssing et al., 2011). The reduction to Cr(III) is associated with a substantial isotope fractionation, which has shown to vary between -0.4 and -5‰ ($\Delta Cr_{Cr(VI)aq}^{Cr(III)sed}$) (Ellis et al., 2002; Zink et al., 2010; Døssing et al., 2011; Kitchen et al., 2012; Scheiderich et al., 2015). The variability in the fractionation likely a function of the reduction process (e.g Døssing et al., 2011; Kitchen et al., 2012; Wang et al., 2015). On the other hand, the fractionation of Cr(III) oxidation is less constrained. However, the limited data available suggest the fractionation cannot be explained by a single kinetic process (Bain and Bullen, 2005; Zink et al., 2010). Studies have shown that as a result of the heterogeneous and variable $\delta^{53}\text{Cr}$ (0.1‰ and 1.8‰) in seawater, there exist a negative correlation between $\delta^{53}\text{Cr}$ and total Cr concentration (Bonnand et al., 2013; Scheidrerich et al., 2015;

Goring-Harford et al., 2018). This in part can be due to the reduction of Cr(VI) to Cr(III) in surface waters and reoxidation of Cr (III) in the deep-water (Scheidrerich et al., 2015). Experimental studies on carbonates show that Cr is incorporated in the calcite lattice of carbonates without changing its oxidation state (Hua et al., 2007; Tang et al., 2007), thus the chromate ion of marine carbonates can be used to track the seawater $\delta^{53}\text{Cr}$.

In seawater, uptake of Cr is complicated as both the process and fractionation factor are not well constrained. This is because the fractionation factor can be affected by a myriad of things including the redox state, presence of ferrous iron (Reinhard et al., 2014), or duration and length of transportation in the water column (see Holmden et al., 2016 for a summary on fractionation effects on carbonate $\delta^{53}\text{Cr}$). However, biologically produced carbonates are isotopically lighter in $\delta^{53}\text{Cr}$ than seawater thus suggesting a reduction of Cr(VI) to Cr(III). Using the Holmden et al. (2016) model, this process can be rationalized as uptake of Cr(VI) into carbonate sediments with a fractionation factor that promotes the formation of isotopically light Cr(III). However, the size of the fractionation factor or the net effect of the fractionation is not known. This has also been demonstrated in the Great Barrier Reef by Farkas et al., (2019) that the uptake of Cr by the carbonates is isotopically light. Thus, demonstrating the possibility that carbonates in some circumstances can record the $\delta^{53}\text{Cr}$ value of seawater if the carbonates are overprinted without much net fractionation.

Therefore, during OAE 2, it can be expected that the increased supply of Cr(VI) to the ocean will be reduced to Cr(III) and thus decrease the chromate inventory. This, in turn, should be reflected in a lower Cr concentration and higher $\delta^{53}\text{Cr}$. However, two previous studies tested this and showed this not to be the case (e.g., Holmden et al., 2016;

Wang et al., 2016). This led to the conclusion that the unexpected behavior of the carbonate $\delta^{53}\text{Cr}$ in part could be due to the increasing supply of hydrothermal sourced Cr(III) from hydrothermal LIP activity during OAE 2 (Holmden et al., 2016). Thus, if the negative carbonate $\delta^{53}\text{Cr}$ excursion is due to LIP-derived Cr(III) with low $\delta^{53}\text{Cr}$, the interval where the LIP eruptions begin in the Portland core has now been shown by Jones et al. (2020) to have been affected by a 60 kyr hiatus. Hence the ability to the $\delta^{53}\text{Cr}$ signal at a crucial part of volcanism is missing in the Portland core. The stratigraphic completeness of the Iona-1 and the smooth gradual decrease of initial $^{187}\text{Os}/^{188}\text{Os}$ recorded at the onset of OAE 2 (Fig. 3.3) which has been interpreted to signify the onset of LIP volcanism also speaks to the stratigraphic completeness of the Iona-1 record. Hence, this study will also understand the relationship between the onset of volcanism and decrease in carbonate $\delta^{53}\text{Cr}$ that was observed in both the Portland (Holmden et al., 2016) and ODP 1258 (Wang et al., 2016).

Also, the new high-resolution carbonate $\delta^{53}\text{Cr}$ curve produced from the Iona-1 core uses a weak acid leaching technique to target only the carbonate fraction and minimize any detrital contribution as high Al corrections have been shown by Holmden et al. (2016) to affect the carbonate $\delta^{53}\text{Cr}$ curve. This in principle produces a cleaner record of the inferred ocean $\delta^{53}\text{Cr}$ signal and avoids the need for a silicate contamination correction. Avoiding a detrital correction on the data, especially an Al correction is important because the Al correction introduces assumptions that may not be right. For example. it assumes that all Al leached comes from clay or a soluble non-carbonate mineral and also assumes that Cr is leached at a ratio proportional to Al (e.g., Holmden et al., 2016). However, if the source of the Al is different, that is, from seawater then the

corrections are wrong. As a result of the extra uncertainty introduced by the correction, obtaining a signal that doesn't require a correction is crucial.

2.4 Geological setting

The Iona-1 core was drilled on a carbonate shelf at the southern gateway to the WIS in present-day southwest Texas (Fig. 2.1; 29°13.51'N, 100°44.49'W). The core recovered 180 m of Lower Cenomanian to Lower Coniacian marine sediment composed of marls and shales, with intermittent bentonite of the Boquillas Formation of the Eagle Ford Group (Eldrett et al., 2014). Sedimentation was slow and assumed to be relatively continuous during OAE 2 in the study setting (Eldrett et al., 2015a). An age model for the Iona-1 core was constructed from rhythmically deposited inter-bedded limestones and marlstones that were interpreted to reflect orbitally forced on sedimentation patterns and is supported by U-Pb zircon dating of bentonite beds (Eldrett et al. 2014, 2015a, 2015b; Minisini et al., 2017). The interbedded marls are predominantly finely laminated and C-rich in the lower Eagle Ford and become more bioturbated up the core (Eldrett et al., 2014). Stratigraphic patterns in the traces of burrowing organisms and the diversity of benthic foraminifera documented periods of alternating oxic to dysoxic and anoxic bottom waters in the study area during OAE 2. Intervals of C-rich laminated sediment and elevated trace metal nutrients (U, Zn, Co, Ni, Cu, and Mo) are associated with bottom water anoxia (Eldrett et al., 2014; 2015a and Minisini et al., 2017). The depth of deposition is interpreted to be consistently below storm wave base in a restricted, sediment-starved setting (100 to 200m depth; Eldrett et al, 2014).

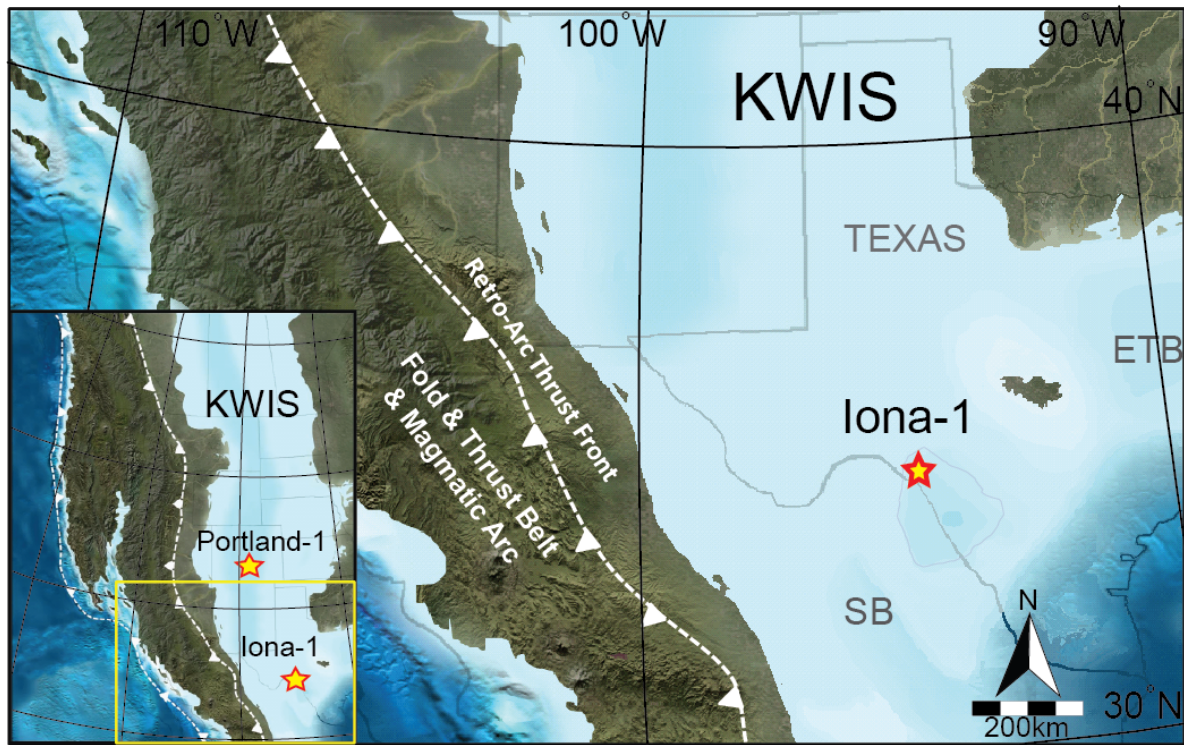


Figure 2.1: Early Turonian paleogeographic map showing the location of Shell Iona-1 and U.S. Geological Survey Portland-1 cores, modified from Eldrett et al., 2014 WIS—Cretaceous Western Interior Seaway.

The onset of the CIE in the Iona-1 core has recently been picked at 112.45 m based on the presumed first increase towards more positive $\delta^{13}\text{C}_{\text{org}}$ values (i.e., Eldrett et al., 2015a; Eldrett et al., 2017; Minisini et al., 2018; Sullivan et al. 2020). However, there is some uncertainty in the exact placement of the start of OAE 2 CIE as the increase in $\delta^{13}\text{C}_{\text{org}}$ is subtle over a few meters reflecting the continuous sedimentation over this interval compared to other sections (i.e., Pueblo, CO, USA). This uncertainty was highlighted by Eldrett et al. (2014; 2015b) with some authors placing the start of the CIE at 110.01m (Jenkyns et al. 2017). This study follows the Jenkyns et al. (2017) placement of the onset of OAE 2 in the Iona-1 core.

A decrease in initial $^{187}\text{Os}/^{188}\text{Os}$ begins ~60 kyr before the onset of the positive CIE that traditionally marks the base on OAE 2 and, consistent with recently published Os isotope evidence supporting a volcanic trigger hypothesis for OAE 2 (DuVivier et al., 2014, Jones et al., 2020). The carbonate fraction of the sediment is mostly original low magnesium calcite mud derived from planktic foraminifera and calcispheres. Further details on the sedimentology, stratigraphy, and hydrographic conditions are in Eldrett et al., (2014, 2015a, 2017) and Minisini et al. (2017).

2.5 Analytical methods

2.5.1 Sample preparation

Rock samples from core materials were hand powdered in an aluminum oxide mortar and pestle at the University of Houston. At the Saskatchewan Isotope Laboratory, one-half to one gram of powdered samples were weighed into 50ml centrifuge tubes and leached with 1M ammonium acetate solution for 12hours at room temperature. The

acetate leachates were centrifuged, decanted, and dried. The residues were rinsed 3 times with ultrapure water, then dissolved with acetic acid to extract the carbonate portions from the rocks, and then dried. These residues were then re-dissolved in 3N HNO₃ and dried down on a hot plate at 80°C. This process was repeated three times to ensure any remaining acetate was decomposed. The resulting residues were dissolved in 0.5N HNO₃ and transferred to new pre-weighed acid cleaned 50ml centrifuge tubes to make a stock solution. Additional details of the dissolution technique are published elsewhere (Nana Yobo et al., 2021).

About 5ml of the solution was then aliquoted for trace element analysis by ICP-MS at the Saskatchewan Research Council analytical lab to determine element concentrations. The concentrations of Cr in the sample were then used to calculate the amount of ⁵⁰Cr-⁵⁴Cr spike to be added to the solution before being processed for Cr isotopes.

2.5.2 Chromium isotope analysis

A ⁵⁰Cr-⁵⁴Cr double spike was added to ~300ng of Cr aliquoted from each stock solution. The double spike composition is reported in Scheiderich et al. (2015). Following methods described in Holmden et al. (2016), Fe (III) was added to the solutions, then ultrapure NH₄OH to precipitate Fe(III)-hydroxides and scavenge the Cr(III) at a pH of ~ 8. The samples were agitated on a shaker table for 1 hour, then centrifuged and the supernatant decanted. The iron cake was subsequently dissolved in 6N HCl. A two-step column chemistry procedure was used to purify Cr. The solution containing Cr(III) in 6N HCl was passed through a column containing 2ml of Bio-Rad

AG 1-X8 anion exchange resin. Cr(III) elutes from this column in strong HCl and the Fe(III) is retained. The eluted Cr(III) was dried and re-dissolved in 0.5N HNO₃ and loaded onto to 1.5ml Bio-Rad AG 50-X8 cation resin to purify Cr from matrix cations.

The Cr isotope measurements were performed on a Thermo Fisher Scientific Triton instrument in the Saskatchewan Isotope Laboratory, University of Saskatchewan, SK, Canada, using a dynamic multi-collection routine (Scheiderich et al., 2015). The spiked sample measurements were corrected for instrumental mass bias and small contributions of the tracer, and the ⁵³Cr/⁵²Cr ratios reported in the conventional delta (δ) notation, where $\delta^{53}\text{Cr} = [({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{sample}} / ({}^{53}\text{Cr}/{}^{52}\text{Cr})_{\text{standard}} - 1] \times 1000$. The $\delta^{53}\text{Cr}$ value measured for a stock solution of NIST 3112a is $-0.079 \pm 0.05\text{‰}$ (2σ, n =15),

2.5.3 Trace element analysis

The rare earth element (REE) concentrations were determined on an Agilent QQQ ICP-MS, at the University of Houston. Analytical uncertainty is generally better than $\pm 5\%$ 1σ, monitored by repeated analysis of an internal standard.

2.5.4 Cerium and Eu anomalies

Cerium data from carbonates have been used to monitor changes in redox conditions in seawater in the geological past (e.g Webb and Kamber, 2000; Nothdurft et al., 2004; Ling et al., 2013; Tostevin et al., 2016; Zhou et al., 2016). Unlike all other REEs which have one valence state of +3 (exception is Eu with +2 and +3, see below), Ce has two valence states: Ce (III) and Ce (IV). The Ce anomaly, when observed in

sediments, is typically the result of oxidation of Ce (III) to Ce (IV) that subsequently leads to the depletion of Ce relative to La, Pr, and Nd. The preferential adsorption of Ce(IV) with Mn oxides and Fe hydroxides leaves seawater depleted in Ce relative to its neighboring REE (German and Elderfield, 1990). Carbonate sediments deposited beneath well-oxygenated waters exhibit negative Ce-anomalies, while carbonates deposited beneath anoxic seawater show positive or no Ce-anomalies (De Baar et al., 1988). Hence Ce anomalies in marine carbonates can be used to trace the redox state of the depositional waters. These are reported as Ce/Ce* values, which are approximately 1.0 in anoxic waters, 0.5–1.0 in hypoxic waters, and lower than 0.5 in oxic waters (Zhou et al., 2016). The Ce anomaly was calculated using Lawrence et al. (2006) equation where $Ce/Ce^* = [Ce/(Pr \times (Pr/Nd))]_{PAAS}$.

In addition to Ce, Eu is also redox-sensitive. The europium anomaly relative to other REE arises from the reduction of Eu(III) to Eu(II) in reducing settings and high-temperature environments (Elderfield, 1988; Sverjensky, 1984; Bau, 1991). Thus, the reduction of Eu(III) to Eu(II) increases with increasing temperature (Uysal and Golding, 2003). Slightly positive Eu anomalies are sometimes present in seawater and larger positive Eu anomalies can occur where seawater is mixing with hydrothermal fluids (Meyer et al., 2012). The Eu anomaly is calculated as $Eu/Eu^* = [Eu/(Sm^2 \times Tb)^{1/3}]_{PAAS}$. The Ce and Eu anomaly data produces values that are equal to 1 or less than or equal to 1. A value of 1 signifies no anomaly while values less than or greater than 1 mean there is an anomaly, with the values greater than one signifying an addition of excess Ce or Eu into the seawater.

2.6 Results

The $\delta^{53}\text{Cr}$ values and Cr concentrations for the carbonate fractions of the Iona-1 core are listed in Table 2.1. The carbon isotope excursion (CIE) is traditionally interpreted to mark the onset of OAE 2. A negative excursion in $\delta^{53}\text{Cr}$ values is recorded in the carbonate fraction of the sediment during OAE 2 (Fig. 2.2). The excursion begins slightly before the onset of the C isotope excursion with $\delta^{53}\text{Cr}$ values declining from a fairly uniform background value of +1.7‰. The peak negative values reach a minimum of -0.04‰ stratigraphically just above the start of the peak interval of positive carbon isotope excursion at 104 m. At 105 m, the $\delta^{53}\text{Cr}$ values slowly start to recover to pre-OAE 2 values (Fig. 2.2). The decrease in the $\delta^{53}\text{Cr}$ occurs ~70 kyr after the drop in initial $^{187}\text{Os}/^{188}\text{Os}$ that marks the onset of LIP activity.

Importantly, the stratigraphic trend in carbonate $\delta^{53}\text{Cr}$ values begins an increase in the early part of the section from about 126-115 m before beginning a progressive decrease from 114–103 m. Overall, the decreasing trend in the carbonate $\delta^{53}\text{Cr}$ isotopes from 114–103 m appears to be in steps (Fig. 2.2). These steps correlate to spikes in Os abundance (at 106.1 m and 105 m respectively). The Os abundance spikes (Fig. 2D) have been interpreted to represent pulses in Large Igneous Province (LIP) eruptions (Sullivan et al., 2020).

Ce/Ce*, Eu/Eu*, and REE concentrations are reported in Table 2.2 and 2.3. The Ce/Ce* profile just like the $\delta^{53}\text{Cr}$ (Fig. 2.2) records a shift to more negative Ce/Ce* values but unlike the $\delta^{53}\text{Cr}$, the shift in the Ce/Ce* begins ~200 kyr before the onset of the CIE that marks the onset of OAE 2 and stays negative through the end of OAE 2. The Eu/Eu* on the other hand begins to shift to higher values at the same time as Ce/Ce*

(Fig. 2.2). The Eu anomaly overall shows a positive anomaly and stays positive until throughout the remainder of OAE 2.

Table 2.1: Chromium concentration and isotope data for Iona 1 core

Depth	Carb Weight fraction	Cr ID (ppm)	Al (ppm)	Ti (ppm)	$\delta^{53}\text{Cr}$	2se	Corrected For Al			Corrected For Ti		
							$\delta^{53}\text{Cr}$ corr.	Cr carb (ppm)	Detrital fract.	$\delta^{53}\text{Cr}$ corr.	Cr carb	Detrital fract.
85.31	0.95	1.19	75	0.01	1.10	0.11	1.13	1.16	0.03	1.10	1.19	0.00
89.32	0.42	1.40	80	0.00	1.32	0.03	1.36	1.36	0.03	1.32	1.40	0.00
90.57	0.59	1.23	146	0.13	1.41	0.02	1.50	1.16	0.06	1.41	1.23	0.00
90.57	0.44	2.36	44	0.00	1.41	0.02	1.43	2.34	0.01	1.41	2.36	0.00
90.83	0.17	0.33	35	0.00	1.61	0.02	1.70	0.32	0.05	1.61	0.33	0.00
92.73	0.43	0.66	359	0.30	0.93	0.05	1.30	0.49	0.26	0.94	0.66	0.01
93.44	0.32	0.52	71	0.00	1.33	0.03	1.43	0.49	0.07	1.33	0.52	0.00
94.22	0.43	0.76	58	0.03	1.25	0.06	1.30	0.74	0.04	1.25	0.76	0.00
94.73	0.37	0.62	76	0.00	1.29	0.02	1.38	0.59	0.06	1.29	0.62	0.00
95.32	0.20	0.32	44	0.00	1.00	0.01	1.08	0.30	0.07	1.00	0.32	0.00
96.10	0.59	1.34	100	0.04	0.91	0.04	0.95	1.30	0.04	0.91	1.34	0.00
97.41	0.47	1.05	73	0.00	0.99	0.03	1.03	1.01	0.03	0.99	1.05	0.00
98.08	0.36	0.37	97	0.00	0.85	0.03	0.99	0.32	0.13	0.85	0.37	0.00
98.56	0.41	1.62	61	0.06	1.72	0.04	1.75	1.59	0.02	1.72	1.62	0.00
100.30	0.32	1.69	183	0.09	0.33	0.06	0.35	1.60	0.05	0.33	1.69	0.00
100.90	0.51	1.01	236	0.83	0.23	0.02	0.28	0.90	0.11	0.24	1.00	0.01
101.83	0.25	0.66	50	0.25	0.03	0.03	0.04	0.64	0.04	0.03	0.66	0.00
102.21	0.33	1.34	334	1.25	0.22	0.02	0.27	1.18	0.12	0.23	1.33	0.01
102.63	0.19	1.06	132	0.00	-0.01	0.02	-0.01	1.00	0.06	-0.01	1.06	0.00
102.95	0.29	2.30	276	0.00	-0.09	0.07	-0.09	2.17	0.06	-0.09	2.30	0.00

103.33	0.15	2.31	1261	0.00	-0.12	0.02	-0.11	1.70	0.26	-0.12	2.31	0.00
103.44	0.63	4.45	37	0.12	0.06	0.02	0.06	4.44	0.00	0.06	4.45	0.00
103.54	0.19	1.23	105	0.00	-0.04	0.02	-0.04	1.18	0.04	-0.04	1.23	0.00
104.18	0.43	0.90	54	0.05	0.26	0.14	0.28	0.87	0.03	0.26	0.90	0.00
104.83	0.50	0.72	290	0.67	0.98	0.04	1.24	0.58	0.19	0.99	0.71	0.01
105.68	0.40	0.66	73	0.00	0.74	0.02	0.78	0.63	0.05	0.74	0.66	0.00
105.96	0.42	0.34	70	0.30	0.74	0.05	0.83	0.31	0.10	0.75	0.34	0.01
106.45	0.33	1.02	254	1.10	0.83	0.03	0.96	0.90	0.12	0.84	1.01	0.01
106.50	0.45	1.17	72	0.00	1.35	0.02	1.40	1.14	0.03	1.35	1.17	0.00
106.94	0.51	0.49	152	0.03	0.68	0.11	0.82	0.42	0.15	0.68	0.49	0.00
107.17	0.55	1.12	153	0.41	0.72	0.02	0.78	1.04	0.07	0.72	1.11	0.00
108.77	0.43	0.27	111	0.29	0.99	0.09	1.27	0.21	0.20	1.01	0.26	0.01
109.22	0.45	0.72	28	0.00	0.87	0.03	0.89	0.71	0.02	0.87	0.72	0.00
110.01	0.43	1.95	31	0.00	1.75	0.03	1.76	1.94	0.01	1.75	1.95	0.00
110.49	0.43	1.86	71	0.27	1.86	0.03	1.89	1.83	0.02	1.86	1.86	0.00
111.36	0.47	2.65	115	0.25	1.59	0.05	1.62	2.60	0.02	1.59	2.65	0.00
111.88	0.36	1.23	90	0.89	1.60	0.05	1.67	1.19	0.04	1.62	1.22	0.01
112.77	0.41	1.30	167	0.00	1.73	0.03	1.85	1.22	0.06	1.73	1.30	0.00
113.42	0.21	0.58	55	0.00	1.99	0.02	2.09	0.55	0.05	1.99	0.58	0.00
114.04	0.65	1.29	73	0.09	1.66	0.03	1.71	1.26	0.03	1.66	1.29	0.00
114.50	0.21	2.58	50	0.00	1.93	0.04	1.95	2.56	0.01	1.93	2.58	0.00
115.45	0.41	0.60	305	0.31	1.72	0.02	2.31	0.46	0.24	1.73	0.60	0.01
119.77	0.49	2.15	248	0.56	1.59	0.02	1.69	2.03	0.06	1.60	2.14	0.00
120.40	0.45	1.35	28	0.41	1.55	0.11	1.57	1.33	0.01	1.56	1.34	0.00
121.09	0.44	3.00	260	0.42	1.76	0.02	1.84	2.87	0.04	1.77	2.99	0.00
123.14	0.41	1.84	617	0.55	1.47	0.02	1.77	1.54	0.16	1.47	1.83	0.00
123.68	0.54	1.00	94	0.18	1.54	0.02	1.62	0.96	0.05	1.55	1.00	0.00

124.03	0.45	1.78	373	0.45	1.54	0.09	1.73	1.61	0.10	1.55	1.78	0.00
125.13	0.43	1.90	59	0.00	1.73	0.04	1.76	1.87	0.01	1.73	1.90	0.00
127.31	0.42	1.55	434	0.47	1.46	0.02	1.70	1.34	0.13	1.46	1.54	0.00

¹Gravimetric determinations after acidification to remove carbonate minerals.

² Cr concentration measured by isotope dilution thermal ionization mass spectrometry.

³ Concentration reported on a carbonate basis (i.e., the weight of residue is subtracted from the total weight of the sample).

⁴ Measured $\delta^{53}\text{Cr}$ on the acid-soluble fraction of the samples.

⁵ 2 s.e. is twice the standard error of the mean derived from the mass spectrometric measurements.

Table 2.2: Measured REE concentration of carbonate fraction (ppm) from the Iona-1 core

Stratigraphic height	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
80.25	1.93	3.47	0.44	1.65	0.35	0.09	0.34	0.05	0.33	0.07	0.19	0.03	0.18	0.02	2.06
85.31	3.48	6.68	0.81	2.98	0.59	0.15	0.57	0.09	0.54	0.10	0.30	0.04	0.30	0.04	3.08
89.32	4.42	7.19	0.91	3.40	0.68	0.16	0.72	0.11	0.68	0.13	0.40	0.06	0.42	0.06	4.35
90.57	3.28	5.33	0.65	2.36	0.47	0.11	0.50	0.07	0.48	0.10	0.30	0.04	0.30	0.05	2.93
92.73	5.61	9.37	1.10	4.11	0.82	0.19	0.87	0.13	0.84	0.18	0.53	0.08	0.51	0.08	5.10
93.44	2.36	3.97	0.47	1.77	0.36	0.09	0.37	0.06	0.33	0.07	0.21	0.03	0.21	0.03	2.38
94.22	3.41	5.45	0.67	2.62	0.52	0.12	0.54	0.08	0.53	0.11	0.32	0.04	0.30	0.05	3.83
94.73	2.48	4.31	0.53	1.99	0.41	0.10	0.40	0.06	0.37	0.07	0.22	0.03	0.22	0.03	2.37
96.10	2.48	4.03	0.49	1.84	0.36	0.09	0.38	0.06	0.34	0.07	0.20	0.03	0.20	0.03	2.31
97.41	2.10	3.18	0.41	1.53	0.31	0.08	0.31	0.05	0.28	0.06	0.17	0.02	0.17	0.02	1.93
98.08	3.43	5.96	0.70	2.54	0.49	0.10	0.50	0.07	0.44	0.09	0.25	0.03	0.26	0.04	2.77
98.56	3.80	5.90	0.70	2.58	0.52	0.11	0.51	0.07	0.46	0.09	0.27	0.04	0.28	0.04	3.15
100.30	3.09	5.36	0.61	2.26	0.45	0.11	0.43	0.06	0.40	0.08	0.23	0.03	0.22	0.03	2.48
100.90	3.27	5.44	0.64	2.44	0.50	0.11	0.57	0.09	0.57	0.12	0.37	0.05	0.36	0.05	4.10
102.21	1.07	2.05	0.27	1.10	0.28	0.09	0.34	0.06	0.43	0.09	0.30	0.04	0.31	0.04	2.58
102.95	1.50	2.99	0.39	1.56	0.38	0.12	0.43	0.08	0.51	0.10	0.30	0.04	0.31	0.05	2.77
103.44	1.80	2.85	0.35	1.34	0.31	0.10	0.42	0.07	0.53	0.12	0.39	0.06	0.41	0.06	3.56
104.44	3.77	6.78	0.80	2.91	0.61	0.17	0.65	0.11	0.69	0.14	0.39	0.06	0.38	0.05	3.02
104.83	2.36	3.92	0.47	1.76	0.34	0.08	0.34	0.05	0.32	0.06	0.17	0.02	0.17	0.02	1.93
105.68	5.53	9.79	1.12	3.96	0.77	0.16	0.74	0.11	0.70	0.14	0.42	0.06	0.42	0.06	3.04
105.96	3.64	5.90	0.66	2.44	0.44	0.10	0.43	0.06	0.37	0.07	0.21	0.03	0.18	0.03	2.68
106.45	2.38	4.56	0.53	1.98	0.41	0.11	0.40	0.06	0.38	0.07	0.21	0.03	0.21	0.03	2.16
106.50	4.82	9.13	1.04	3.72	0.75	0.17	0.77	0.13	0.78	0.16	0.46	0.07	0.43	0.07	3.46

106.94	3.80	7.20	0.77	2.82	0.54	0.13	0.55	0.08	0.53	0.11	0.31	0.04	0.29	0.04	3.25
107.17	3.58	7.29	0.76	2.74	0.55	0.14	0.53	0.08	0.50	0.10	0.28	0.04	0.27	0.04	3.09
108.77	3.55	6.52	0.69	2.50	0.48	0.10	0.47	0.07	0.45	0.09	0.28	0.04	0.29	0.04	3.16
109.22	6.04	10.46	1.12	3.82	0.73	0.14	0.77	0.12	0.83	0.18	0.56	0.09	0.61	0.09	4.25
110.01	4.77	8.21	0.89	3.08	0.59	0.13	0.64	0.11	0.71	0.15	0.45	0.07	0.44	0.07	3.68
110.49	5.37	8.42	0.91	3.36	0.60	0.17	0.68	0.11	0.70	0.15	0.47	0.07	0.46	0.07	5.42
111.36	3.13	5.23	0.57	2.09	0.39	0.09	0.39	0.06	0.36	0.07	0.23	0.03	0.23	0.03	2.51
111.88	3.68	6.69	0.75	2.69	0.54	0.13	0.49	0.07	0.44	0.09	0.26	0.04	0.25	0.04	2.80
112.45	5.29	7.83	0.81	2.88	0.52	0.13	0.57	0.08	0.55	0.12	0.36	0.05	0.36	0.06	4.19
112.77	5.04	8.85	0.90	3.05	0.55	0.13	0.50	0.07	0.45	0.08	0.24	0.04	0.26	0.04	2.71
114.04	3.06	4.05	0.41	1.42	0.25	0.05	0.28	0.04	0.28	0.06	0.20	0.03	0.21	0.03	2.10
115.45	4.60	8.02	0.86	3.02	0.58	0.13	0.57	0.09	0.56	0.12	0.33	0.05	0.33	0.05	2.76
118.16	2.57	3.64	0.42	1.50	0.28	0.07	0.28	0.04	0.28	0.06	0.19	0.03	0.22	0.03	1.71
119.77	3.85	6.40	0.70	2.44	0.47	0.10	0.50	0.09	0.60	0.13	0.42	0.07	0.49	0.08	3.13
120.40	2.57	3.95	0.44	1.65	0.31	0.07	0.30	0.04	0.29	0.06	0.20	0.03	0.22	0.03	2.31
121.09	3.55	5.43	0.60	2.12	0.39	0.08	0.41	0.06	0.42	0.09	0.28	0.04	0.31	0.05	2.21
122.18	2.88	4.30	0.50	1.82	0.32	0.06	0.32	0.05	0.34	0.07	0.23	0.04	0.26	0.04	1.78
123.14	5.86	10.79	1.24	4.34	0.85	0.14	0.76	0.12	0.75	0.16	0.46	0.07	0.51	0.08	3.47
123.68	1.25	1.94	0.22	0.77	0.13	0.02	0.13	0.02	0.12	0.02	0.08	0.01	0.07	0.01	0.81
124.03	4.78	8.95	1.06	3.76	0.74	0.11	0.70	0.11	0.69	0.14	0.42	0.07	0.45	0.07	3.69
125.13	2.92	3.42	0.38	1.41	0.25	0.07	0.29	0.04	0.31	0.07	0.23	0.04	0.27	0.05	2.96
127.31	7.95	13.26	1.45	4.83	0.92	0.14	0.86	0.13	0.85	0.18	0.53	0.09	0.58	0.09	5.33
129.27	2.75	4.97	0.55	1.95	0.37	0.08	0.34	0.05	0.30	0.06	0.18	0.03	0.19	0.03	1.94
130.17	1.71	2.32	0.25	0.89	0.16	0.02	0.15	0.02	0.12	0.03	0.08	0.01	0.08	0.01	1.32

Table 2.3: REE Normalised values to Post Archean Australian Shale (PAAS) and calculated Ce and Eu anomaly.

Stratigraphic height	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y	Ce*	Eu*
80.25	0.05	0.04	0.05	0.05	0.06	0.08	0.07	0.07	0.07	0.07	0.07	0.06	0.06	0.06	0.08	0.85	1.23
85.31	0.09	0.08	0.09	0.09	0.11	0.14	0.12	0.11	0.11	0.10	0.10	0.10	0.11	0.10	0.11	0.87	1.19
89.32	0.12	0.09	0.10	0.10	0.12	0.15	0.15	0.14	0.15	0.14	0.14	0.14	0.15	0.14	0.16	0.81	1.09
90.57	0.09	0.07	0.07	0.07	0.09	0.10	0.11	0.10	0.10	0.10	0.10	0.11	0.11	0.10	0.11	0.89	1.09
92.73	0.15	0.12	0.13	0.12	0.15	0.17	0.19	0.17	0.18	0.18	0.19	0.19	0.18	0.18	0.19	0.86	1.04
93.44	0.06	0.05	0.05	0.05	0.06	0.08	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.09	0.91	1.08
94.22	0.09	0.07	0.08	0.08	0.09	0.11	0.12	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.14	0.82	1.07
94.73	0.06	0.05	0.06	0.06	0.07	0.09	0.09	0.08	0.08	0.07	0.08	0.07	0.08	0.07	0.09	0.87	1.14
96.10	0.06	0.05	0.06	0.05	0.07	0.09	0.08	0.07	0.07	0.07	0.07	0.07	0.07	0.06	0.09	0.88	1.16
97.41	0.05	0.04	0.05	0.05	0.06	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.84	1.16
98.08	0.09	0.07	0.08	0.07	0.09	0.09	0.11	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.92	0.94
98.56	0.10	0.07	0.08	0.08	0.09	0.11	0.11	0.09	0.10	0.09	0.09	0.10	0.10	0.09	0.12	0.90	1.05
100.30	0.08	0.07	0.07	0.07	0.08	0.10	0.09	0.08	0.08	0.08	0.08	0.08	0.08	0.07	0.09	0.94	1.15
100.90	0.09	0.07	0.07	0.07	0.09	0.10	0.12	0.11	0.12	0.12	0.13	0.13	0.13	0.13	0.15	0.88	0.95
102.21	0.03	0.03	0.03	0.03	0.05	0.08	0.07	0.08	0.09	0.09	0.10	0.11	0.11	0.10	0.10	0.77	1.33
102.95	0.04	0.04	0.04	0.05	0.07	0.11	0.09	0.10	0.11	0.10	0.11	0.11	0.11	0.11	0.10	0.78	1.34
103.44	0.05	0.04	0.04	0.04	0.06	0.09	0.09	0.09	0.11	0.13	0.14	0.15	0.14	0.14	0.13	0.87	1.25
104.44	0.10	0.09	0.09	0.09	0.11	0.16	0.14	0.14	0.15	0.14	0.14	0.14	0.14	0.12	0.11	0.91	1.24
104.83	0.06	0.05	0.05	0.05	0.06	0.08	0.07	0.06	0.07	0.06	0.06	0.06	0.06	0.06	0.07	0.90	1.12
105.68	0.14	0.12	0.13	0.12	0.14	0.15	0.16	0.15	0.15	0.14	0.15	0.15	0.15	0.14	0.11	0.92	1.03
105.96	0.10	0.07	0.07	0.07	0.08	0.10	0.09	0.07	0.08	0.07	0.07	0.07	0.06	0.06	0.10	0.96	1.12
106.45	0.06	0.06	0.06	0.06	0.07	0.10	0.09	0.08	0.08	0.07	0.07	0.07	0.07	0.07	0.08	0.92	1.28
106.50	0.13	0.11	0.12	0.11	0.14	0.16	0.17	0.16	0.17	0.16	0.16	0.17	0.15	0.15	0.13	0.93	1.03

106.94	0.10	0.09	0.09	0.08	0.10	0.12	0.12	0.11	0.11	0.11	0.11	0.11	0.10	0.10	0.12	1.00	1.09
107.17	0.09	0.09	0.09	0.08	0.10	0.13	0.11	0.10	0.11	0.10	0.10	0.10	0.10	0.09	0.11	1.04	1.22
108.77	0.09	0.08	0.08	0.07	0.09	0.10	0.10	0.09	0.10	0.09	0.10	0.09	0.10	0.10	0.12	1.03	1.02
109.22	0.16	0.13	0.13	0.11	0.13	0.13	0.16	0.16	0.18	0.18	0.20	0.21	0.22	0.22	0.16	1.02	0.88
110.01	0.12	0.10	0.10	0.09	0.11	0.12	0.14	0.14	0.15	0.15	0.16	0.16	0.16	0.15	0.14	1.02	1.00
110.49	0.14	0.11	0.10	0.10	0.11	0.16	0.15	0.14	0.15	0.15	0.17	0.17	0.16	0.17	0.20	0.96	1.25
111.36	0.08	0.07	0.06	0.06	0.07	0.09	0.08	0.07	0.08	0.08	0.08	0.08	0.08	0.08	0.09	1.00	1.12
111.88	0.10	0.08	0.08	0.08	0.10	0.12	0.10	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.10	0.97	1.20
112.45	0.14	0.10	0.09	0.09	0.09	0.12	0.12	0.11	0.12	0.12	0.13	0.13	0.13	0.13	0.16	1.05	1.14
112.77	0.13	0.11	0.10	0.09	0.10	0.12	0.11	0.09	0.10	0.08	0.09	0.09	0.09	0.09	0.10	1.11	1.18
114.04	0.08	0.05	0.05	0.04	0.04	0.05	0.06	0.05	0.06	0.06	0.07	0.08	0.07	0.08	0.08	1.15	0.95
115.45	0.12	0.10	0.10	0.09	0.11	0.12	0.12	0.12	0.12	0.12	0.12	0.13	0.12	0.12	0.10	1.02	1.01
118.16	0.07	0.05	0.05	0.04	0.05	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.08	0.08	0.06	0.98	1.12
119.77	0.10	0.08	0.08	0.07	0.09	0.09	0.11	0.11	0.13	0.13	0.15	0.17	0.17	0.18	0.12	1.03	0.95
120.40	0.07	0.05	0.05	0.05	0.06	0.06	0.06	0.06	0.06	0.06	0.07	0.07	0.08	0.07	0.09	0.97	1.06
121.09	0.09	0.07	0.07	0.06	0.07	0.08	0.09	0.08	0.09	0.09	0.10	0.11	0.11	0.12	0.08	1.01	0.99
122.18	0.08	0.05	0.06	0.05	0.06	0.06	0.07	0.07	0.07	0.07	0.08	0.09	0.09	0.10	0.07	0.95	0.90
123.14	0.15	0.14	0.14	0.13	0.15	0.13	0.16	0.15	0.16	0.16	0.16	0.18	0.18	0.19	0.13	0.92	0.80
123.68	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.03	0.02	0.03	0.03	1.04	0.70
124.03	0.13	0.11	0.12	0.11	0.13	0.11	0.15	0.14	0.15	0.14	0.15	0.17	0.16	0.16	0.14	0.90	0.74
125.13	0.08	0.04	0.04	0.04	0.05	0.06	0.06	0.06	0.07	0.07	0.08	0.09	0.10	0.11	0.11	0.99	1.16
127.31	0.21	0.17	0.16	0.14	0.17	0.13	0.18	0.17	0.18	0.18	0.19	0.21	0.21	0.21	0.20	0.98	0.73
129.27	0.07	0.06	0.06	0.06	0.07	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.07	0.06	0.07	1.01	1.08
130.17	0.04	0.03	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.05	1.08	0.72

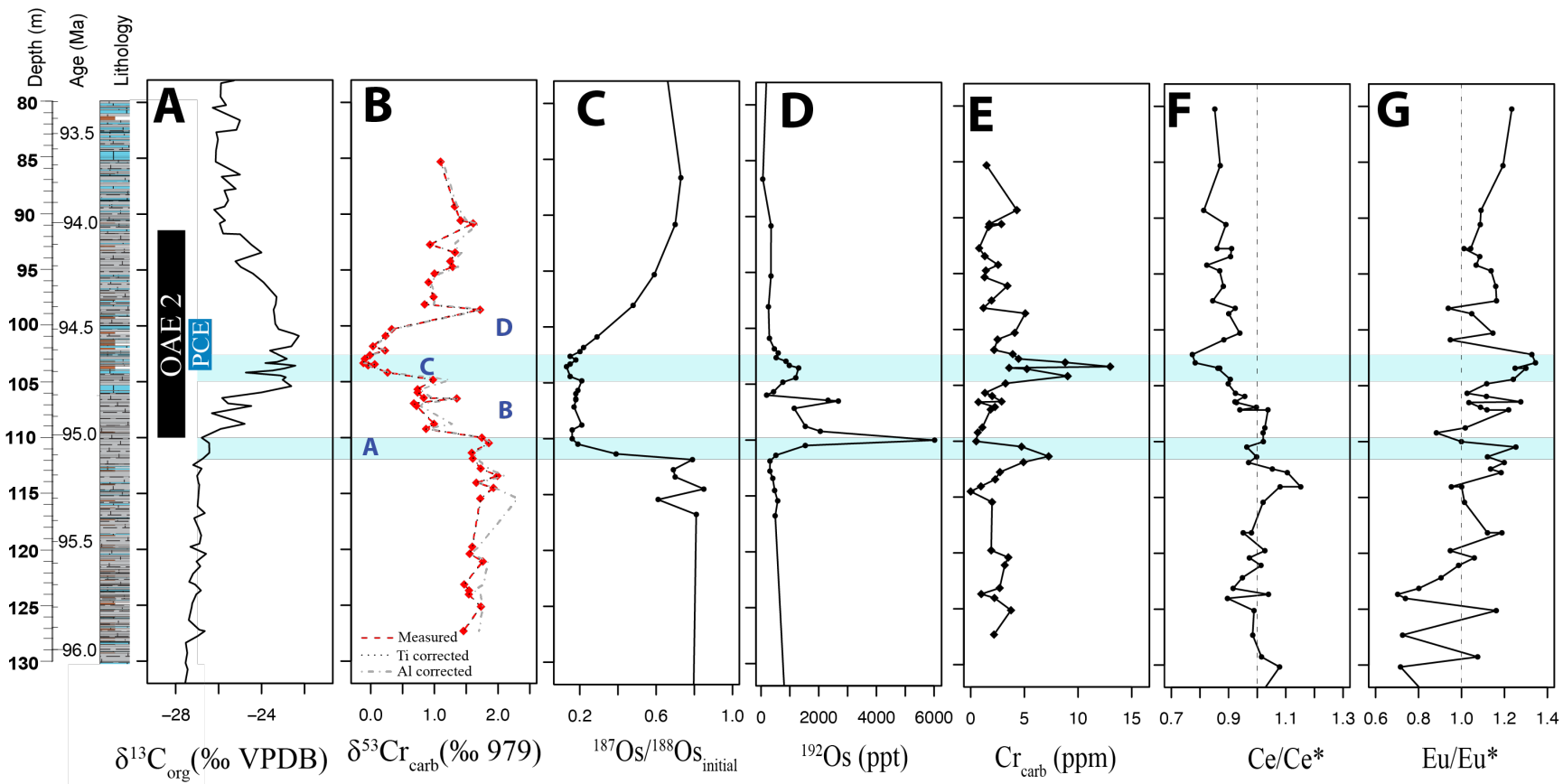


Figure 2.2: Sedimentary $\delta^{53}\text{Cr}$ profile through OAE 2 of the Iona-1 core. The stratigraphic depth, age, and $\delta^{13}\text{C}_{\text{org}}$ (Eldrett et al., 2014), $^{187}\text{Os}/^{188}\text{Os}$ and ^{192}Os concentrations (Sullivan et al., 2020) and measured $\delta^{53}\text{Cr}$ (this study). Also plotted are the Ce/Ce^* and Eu/Eu^* of the carbonate fractions (details on the calculations of the Ce and Eu anomaly are in the text). The dark shade represents the duration of the OAE 2 interval, while the blue shade represents the duration of the Plenus Cold Event (PCE). A represents the delay in onset of negative shift in $\delta^{53}\text{Cr}$ in relation to LIP eruption (70 kyr), as indicated by decrease in $^{187}\text{Os}/^{188}\text{Os}$ and increased Os concentration. B is the first negative shift in Cr isotopes corresponds to the middle of the peak negative shift in Os isotopes. C represents the interval of second shift to lower $\delta^{53}\text{Cr}$ in lower part of the PCE occurs synchronously with increase volcanism as indicated by decrease in $^{187}\text{Os}/^{188}\text{Os}$ and increased Os concentration. Finally, D represents the end of volcanism signaled by rise in $^{187}\text{Os}/^{188}\text{Os}$, which occurs synchronously with rise in $\delta^{53}\text{Cr}$.

2.7 Discussion

2.7.1 Evaluation of the carbonate $\delta^{53}\text{Cr}$ isotope data

Previous work on the Portland core (Fig. 2.1) showed that due to the mixed siliciclastic-carbonate and marl of the sediments, some Cr from Fe oxyhydroxides that were fractionated differently than the Cr in the calcite lattice were likely picked up in the leaching process hence necessitating a detrital correction for the carbonate $\delta^{53}\text{Cr}$ data (Holmden et al., 2016). Hence, the dissolution technique used here (Section 2.4.1) minimizes the detrital Cr corrections a resulting in a cleaner record of sedimentary $\delta^{53}\text{Cr}$ changes surrounding the onset of OAE 2. This is because detrital corrections especially Al usually result in increases to the carbonate $\delta^{53}\text{Cr}$ as the corrections are typically greater than the measurement uncertainties (Holmden et al., 2016). Notwithstanding, a detrital correction was applied to the data to check for any soluble non-carbonate component that may have been released during the ammonium acetate leach, using Al and Ti as monitors of the detrital component. The Al and Ti corrections were performed by multiplying the concentrations of calculated Al and Ti in each sample by the average upper-crust ratios of Cr/Al and Cr/Ti respectively (Table 1). As expected, the Ti corrections are negligible and fall within the uncertainty of the measurements (Table 2.1, Fig. 2.2B). The Al correction is similar to the measured values except for one sample (at 115.45m) which results in a significantly higher carbonate $\delta^{53}\text{Cr}$ of +2.31 relative to the measured value of +1.73‰.

As discussed by Holmden et al., (2016) Al is easy to leach and there is a high concentration of Al in both the detrital (silicates and clay mineral) and authigenic (high concentrations of Al over Cr in seawater of 5–40 nmol/kg and 2–7 nmol/kg, respectively) sources. Thus Holmden et al. (2016) concluded that some of the Al released during leaching could have been authigenic. On that basis the Al correction was negligible. However, here, it is

possible to compare the weak acid leaching method from this study to the technique used in Holmden et al. (2016). The measured data from this study even before any corrections are higher, similar to the corrected values from the Portland core of Holmden et al. (2016) (Fig. 2.3). This illustrates the effectiveness of the leaching method employed here and the ability to have clean carbonate $\delta^{53}\text{Cr}$ values with minimal detrital input of Cr. Also, this illustrates that the Cr isotope correction approach of Holmden et al., (2016) is accurate because they were leaching Al. Hence their corrected values are close to the uncorrected measured carbonate $\delta^{53}\text{Cr}$ values in this study (Fig. 2.3). In this light, all but one of the measured carbonate $\delta^{53}\text{Cr}$ values in the Iona-1 core are not affected by the correction. The elevated Al correction on this one sample (sample at 115.45 m depth, Table 2.1) is interpreted to be an artifact of authigenic Al and is not further considered here. Additionally, in this one instance where the Al correction is large, ignoring the elevated Al corrected data point does not change the overall decreasing trend in the $\delta^{53}\text{Cr}$ profile (Fig. 2.2B).

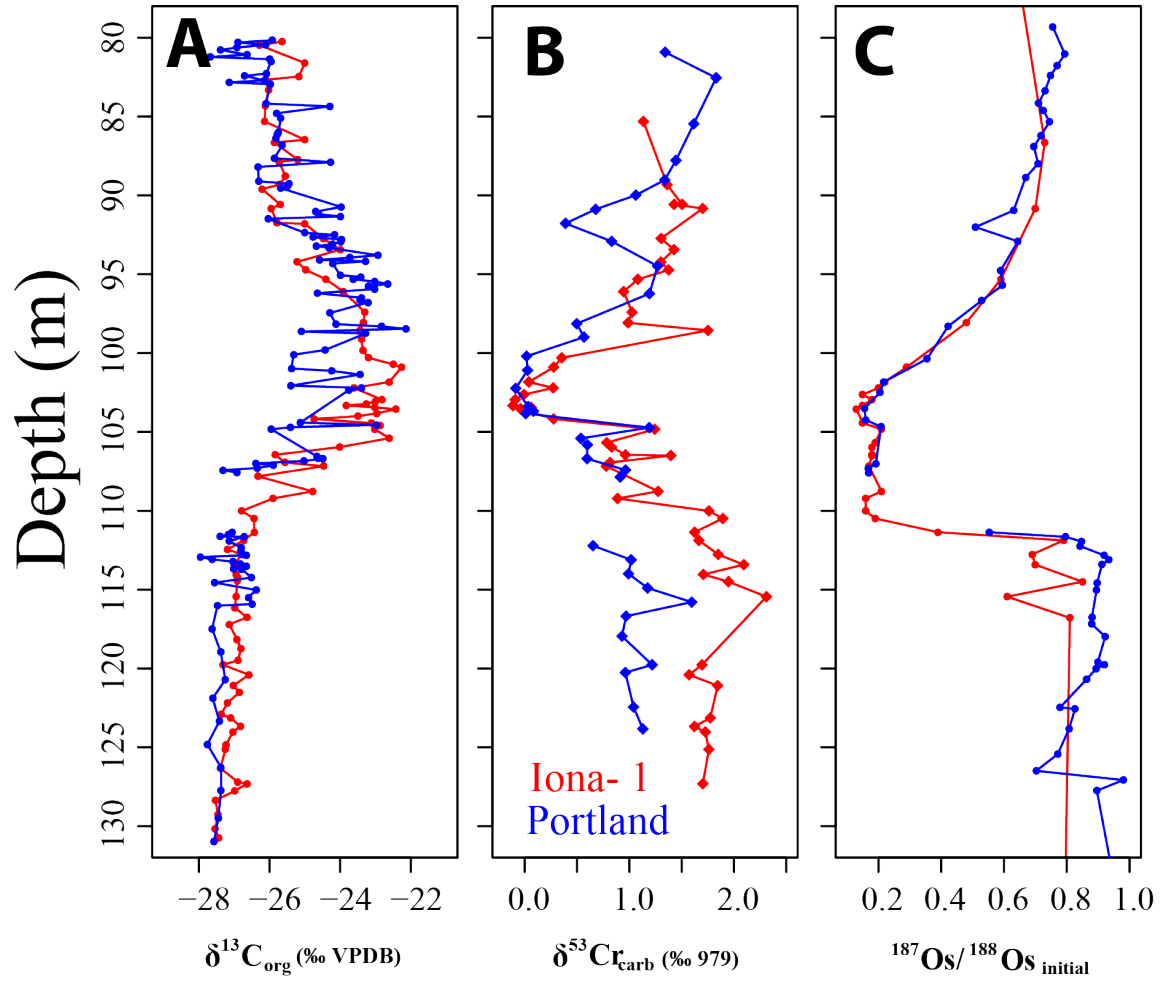


Figure 2.3: Stratigraphic comparison plot between the Iona-1 core and Portland Core A1 corrected carbonate $\delta^{53}\text{Cr}$ values. The stratigraphic height of the Portland core depth was adjusted to account for the ~60 kyr hiatus (Jones et al., 2020) at the onset of OAE 2. Portland core $\delta^{13}\text{C}$ of organic carbon (Sageman et al., 2006), $^{187}\text{Os}/^{188}\text{Os}$ (Du Vivier et al., 2014), and $\delta^{53}\text{Cr}$ (Holmden et al., 2016). Iona $\delta^{13}\text{C}$ (Eldrett et al., 2014), $^{187}\text{Os}/^{188}\text{Os}$ (Sullivan et al., 2020), and $\delta^{53}\text{Cr}$ (this study).

2.7.2 The carbonate $\delta^{53}\text{Cr}$ isotope trend

The negative excursion in $\delta^{53}\text{Cr}$ values progressing from older to younger OAE 2 in the Iona-1 section is consistent with the previously reported trend in carbonate fractions of the WIS in the earlier study of the Portland Core (Holmden et al., 2016) with three important differences. First, the Iona-1 section provides a cleaner and more continuous record of $\delta^{53}\text{Cr}$. Second, the $\delta^{53}\text{Cr}$ excursion appears to start lower in the section, coincident with the shift to unradiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios (Fig. 2.2). In the Portland core, the negative shift in $\delta^{53}\text{Cr}$ appears to begin after the onset of volcanism, but the Portland record is complicated in this interval by sedimentary hiatus (Fig. 3; ~60 kyr, Jones et al., 2020). Thirdly, the carbonate $\delta^{53}\text{Cr}$ values from the Iona-1 core are still slightly higher than those from the Portland core data in the pre-OAE 2 interval (Fig. 2.3). The difference in the carbonate $\delta^{53}\text{Cr}$ values before OAE 2 in these two sections could mean that seawater was different locally between the two locations or the uptake of Cr by the carbonates was fractionated differently. Notwithstanding, the fact that the trend in the carbonate $\delta^{53}\text{Cr}$ values between the Portland and Iona-1 are similar illustrates that both cores are recording a similar signal that is likely not an artifact of stratigraphic fractionation. In other words, the carbonate $\delta^{53}\text{Cr}$ values are recording changes in seawater $\delta^{53}\text{Cr}$ values offset by a fractionation factor. Also, if the secondary uptake of Cr into carbonate sediments is not affected by a fractionation factor change over the OAE 2 interval, then the record of changing carbonate $\delta^{53}\text{Cr}$ can be used to interpret seawater $\delta^{53}\text{Cr}$.

A key observation of the Iona-1 carbonate $\delta^{53}\text{Cr}$ profile is that the Cr isotope response lags behind the Os response by ~70 kyr. This could be an effect of the residence time differences between the two elements. However, the decreasing carbonate $\delta^{53}\text{Cr}$ continues after the onset of CIE at 110.5 m until halfway through the peak CIE interval at 107 m. At 103 m, the carbonate

$\delta^{53}\text{Cr}$ begins to increase while the $^{187}\text{Os}/^{188}\text{Os}$ increases back to pre-OAE 2 values. The recovery of $\delta^{53}\text{Cr}$ which begins at 103 m, falls within a stratigraphic interval called the “benthic oxic zone” (Eldrett et al., 2014). Found within this interval is the Boreal dinocyst *Cyclonephelium compactum*–*C.membraniphorum* (Eldrett et al., 2014) which has been interpreted to indicate the influx of northern water mass southward into the WIS (van Helmond et al., 2013).

This interval is equivalent to the “Plenus Cold Event” (PCE) which has been identified in the European section because of the presence of boreal faunas (Gale and Christensen, 1996; Jenkyns et al., 2017). As a result, Jenkyns et al. (2017) proposed that during the PCE redox-sensitive trace metal that had been previously drawn down and adsorbed onto organic matter and pyrite as a result of the growth of anoxia should be released during this time. That is the PCE serves as a global release of nutrients and heavy metals such as Cr from reoxidation of anoxic marine sediments.

However recent studies by O’Connor et al. (2019) suggest the PCE was dominantly driven by local and not global changes – and by extension, the local cooling response is not uniform, even though there is an inflow of Boreal waters, it was not accompanied by a change in temperature (O’Connor et al., 2019).

If the Jenkyns et al. (2017) hypothesis is correct, and redox-sensitive trace metals are locked into the carbonate sediments during the growth of anoxia and are later on re-release during the PCE, then when it released, the $\delta^{53}\text{Cr}$ should be heavy. However, this is not the case, as, during PCE equivalent interval, the carbonate $\delta^{53}\text{Cr}$ goes negative and not positive. In the Iona-1 record, the PCE equivalent interval also correlates with a spike in ^{192}Os concentration, thus suggesting that LIP activity persisted through the PCE and wasn’t shut down. This is also supported by Nd isotopes data that show an increase in epsilon units during the PCE, inconsistent

with a decrease in volcanism during this time. Thus the carbonate $\delta^{53}\text{Cr}$ further reveals the influence of hydrothermal activity and likely release of Cr(III) into the oceans from a hydrothermal source (Holmden et al., 2016).

Similarly, the Ce/Ce* averages around 1 before the onset of OAE 2 and peaks at 1.2 around ~114 m where $\delta^{53}\text{Cr}$ is at its highest values. After this, Ce/Ce* and $\delta^{53}\text{Cr}$ both generally track each other with progressively decreasing values. The Ce/Ce* values are at their lowest when the $\delta^{53}\text{Cr}$ values are also lowest within OAE 2 at ~105 m. The positive anomaly of Ce/Ce* (values greater than 1) indicate anoxic conditions persisted before and after the onset of OAE 2, until around the onset of the peak CIE at ~106m where a more oxic bottom water condition persisted through the remainder of OAE 2 and beyond in the WIS. The Eu/Eu* begins to show a positive shift (122–118 m) from 0.7 to 1.2, before the onset of OAE 2. In this same interval, the Ce/Ce* is averaging ~ 1. This indicates that the bottom waters moving into the WIS were likely hydrothermally sourced but not very close to the WIS. This is because Eu anomalies are typically interpreted as inherited from igneous sources (Taylor and McLennan 1985). However, the peak Ce/Ce* is coincident with the onset of a persistent positive Eu/Eu* at 114 m. This is consistent with the addition of hydrothermally sourced water into the WIS during this time that was likely responsible for the change in the redox state. This condition of increased hydrothermal influence persists through OAE 2 but slows down around 103m core depth indicated by a drop in Eu/Eu* (values <1) and at the onset of increasing $\delta^{53}\text{Cr}$ values and initial $^{187}\text{Os}/^{188}\text{Os}$ ratios. This interval likely records the maximum influence of the hydrothermal LIP sourcing. This also correlates with one of the peak intervals of Os abundance supporting the increase in hydrothermal influence (Sullivan et al., 2020).

In previous studies, the carbonate $\delta^{53}\text{Cr}$ values in similar OAE 2 sedimentary sequences to that of the Iona-1 core have been described as not meeting the expected behavior of Cr as a redox element (Holmden et al., 2016). This stems from the prediction that carbonate $\delta^{53}\text{Cr}$ values should increase during OAE 2 as a result of reduction of Cr(IV), resulting in a positive excursion in $\delta^{53}\text{Cr}$, instead a negative $\delta^{53}\text{Cr}$ that was measured (Holmden et al., 2016; Wang et al., 2016). The Iona-1 the $\delta^{53}\text{Cr}$ record can be divided into two parts. The first part represents the expected response (126–114m depth) and the second part represents the unexpected response (114–91 m depth). In the first part, the Ce/Ce* anomalies average around 1 and then show an increase to 1.2, possibly signally the onset of local anoxia, where an increased rate of removal of the light ^{52}Cr isotope is expected. This in turn would drive down the Cr abundance and result in higher $\delta^{53}\text{Cr}$ values (Holmden et al., 2016). In this interval, the Iona-1 record for $\delta^{53}\text{Cr}$ is responding as should be expected with a slow but progressive increase in $\delta^{53}\text{Cr}$ (+1.5 to +2‰). However, as LIP eruptions begin, coincident with pulses defined by increases in Os abundances and decreasing initial $^{187}\text{Os}/^{188}\text{Os}$ (Fig. 2), this results in an increase mixture of hydrothermal fluids (supported by positive Eu/Eu*) with the ocean bottom water. In this case, LIP-derived Cr now begins to saturate the system. At which point, the expected response of increasing carbonate $\delta^{53}\text{Cr}$ wanes because of increased addition of LIP-derived Cr(III) and consequent lighter carbonate $\delta^{53}\text{Cr}$ (e.g. Holmden et al., 2016).

2.7.3 Implications for the onset of OAE 2 and timing of deoxygenation

OAE 2 has traditionally been identified by the characteristic shift to higher values of $\delta^{13}\text{C}$. However, based on the synchronicity in the Ce/Ce* and Eu/Eu* in the Iona-1 core sequence, a change in the redox state of the ocean as well as mixing with hydrothermally sourced fluids into the system began about 200 kyr (114–110m) before the CIE and the decrease in initial $^{187}\text{Os}/^{188}\text{Os}$. This indicates that locally, anoxia in the WIS began well before a recognizable change in global $\delta^{13}\text{C}$ and $^{187}\text{Os}/^{188}\text{Os}$ records. The observed delayed response in Os and C isotope systems may be the result of their long residence times of 3 – 50 kyr (Oxburgh 2001) and 100 kyr (Walker 1986) respectively, compared to the much shorter residence time of those for Ce and Eu of 50-100 and 320-800 years (Alibo and Nozaki 1999), in the ocean. Also, the fact that the Iona-1 carbonate $\delta^{53}\text{Cr}$ values are about 0.5‰ heavier than those in the Portland core before the onset of OAE 2 marked by the CIE (Fig. 3), maybe an effect of uptake of Cr fractionation in the carbonate between the two different locales.

2.8 Conclusion

The Iona-1 core from WIS has a smooth and more complete record of the carbonate $\delta^{53}\text{Cr}$ that was previously obtained. The $\delta^{53}\text{Cr}$ values (Al corrected) before OAE 2 show a progressive, gradual increase from +1.5 to + 2‰). This increase broadly represents the response of carbonate $\delta^{53}\text{Cr}$ during increased anoxia in the WIS waters. About 200 kyr before the onset of the CIE, carbonate $\delta^{53}\text{Cr}$ values begin to record a trend progressively lower. This trend continues until the middle peak interval of CIE at 103m. The onset of this negative carbonate $\delta^{53}\text{Cr}$ excursion lags behind the decrease in $^{187}\text{Os}/^{188}\text{Os}$ values by 70 kyr but signifies LIP volcanism and the influx of LIP-derived Cr(III) into the WIS waters. At 105m (94.7Ma) the carbonate $\delta^{53}\text{Cr}$ values

begin to gradually increase and continues until the end of the OAE 2 at 93.97Ma. The onset of increasing $\delta^{53}\text{Cr}$ values also coincides with the wanning of hydrothermal influence which is marked by the progressive increase of initial $^{187}\text{Os}/^{188}\text{Os}$ to values before OAE 2. Importantly, the Ce/Ce* and Eu/Eu* values reinforce the observations recorded in the carbonate $\delta^{53}\text{Cr}$ and show that anoxia started in the WIS about 250 kyr in WIS before the onset of the CIE. The Eu/Eu* values likely indicate that the onset of anoxia was associated with the influx of hydrothermally-sourced fluids into the WIS.

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CHAPTER 3: STABLE CA AND SR ISOTOPE RESPONSE DURING OCEAN ANOXIC EVENT 2

3.1 Abstract

The Cretaceous Ocean Anoxic Events (OAEs), amongst the largest climatic perturbations in the Phanerozoic, resulted in strong biogeochemical changes within the Earth's surface environment. These events subsequently led to the deposition and preservation of unusually large amounts of organic matter that are now preserved as black shale deposits. The organic matter is characterized by positive $\delta^{13}\text{C}$ excursions, both in marine and subaerial environments. Increased volcanic activity has been linked to OAEs as an initial forcing mechanism that resulted in such significant global paleoclimatic change, as well as increased continental weathering activity, and increased ocean productivity. The Ca isotope compositions of carbonates have been used during OAE 2, which occurred during Cenomanian-Turonian times, to reconstruct the drivers of the environmental change associated with this OAE. However, a discrepancy still exists on the $\delta^{44/40}\text{Ca}$ isotope response during OAE 2. In this study, a new $\delta^{44/40}\text{Ca}$ record is generated in a black shale-marl-limestone succession across OAE 2 from the Iona-1 core collected from the Eagle Ford Formation in Texas. The section was deposited in the Cretaceous Interior Seaway (WIS). The $\delta^{44/40}\text{Ca}$ data are paired with $\delta^{88/86}\text{Sr}$ to examine changes and fluctuations recorded during this period.

The $\delta^{44/40}\text{Ca}$ results vary from -1.63 ± 0.02 to -1.29 ± 0.03 ‰ ($\pm 2\text{SE}$) and show a positive excursion similar to Portland core also deposited in the WIS. The new data from the Iona-1 core fills in a time gap that is not captured by the Portland core because of a hiatus in this section at the onset of the OAE 2. Hence the Iona-1 core presents a complete record of the $\delta^{44/40}\text{Ca}$ response during OAE 2. The $\delta^{88/86}\text{Sr}$ data shows a trend that differs from the $\delta^{44/40}\text{Ca}$ trend. This is especially around the onset of OAE 2. This is followed by trends that track each other later on

during OAE 2. However, the low resolution of the data, necessitates additional measurements be obtained to get a complete record of $\delta^{88/86}\text{Sr}$ during OAE 2 as well as to elucidate the precipitation rate effect. The preliminary results show that syn-depositional diagenesis not weathering played a role in the $\delta^{44/40}\text{Ca}$ recorded in the Iona-1 core, thereby highlighting hydrothermal interaction.

3.2 Introduction

Ocean anoxic events (OAE) are amongst the best-studied perturbations of the global carbon cycle in Earth's history. These events are identified in the rock record by elevated $\delta^{13}\text{C}$ values, which signals major perturbations to the Earth's exogenic C cycle from increased organic carbon burial (Schlanger and Jenkyns 1976; Sageman et al., 2006). One of the most studied examples is Ocean Anoxic Event 2 (OAE 2) spanning the Cenomanian-Turonian boundary (CTB) in the Late Cretaceous. Two factors contribute to increased organic carbon burial: (1) higher preservation at the sediment-water interface, which is enhanced during periods of expanded bottom water anoxia in the oceans (e.g., Ostrander et al., 2017), and/or (2) increased exports of primary produced organic matter from the photic zone, which is enhanced during periods of increased nutrient availability in the oceans (Jenkyns, 2010 and references therein).

Because OAE involves the widespread development of oxygen-deficient water masses, many redox-sensitive isotope systems were potentially perturbed in the global ocean during these intervals. Hence, records of isotopic proxies that are sensitive to changes in weathering, hydrothermal activity, and redox conditions have been the focus of frequent studies (e.g. Adams et al., 2010; Jenkyns et al., 2010; Blättler et al., 2011; Pogge von Strandmann et al., 2013; Holmden et al., 2016; Ostrander et al., 2017; Owens et al., 2018; Them et al., 2018). Calcium isotopes have

been used to identify and quantify geochemical and impact of environmental changes in the geologic past (e.g. De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005; Farkaš et al., 2007; Sime et al., 2007; Blättler et al., 2012; Holmden et al., 2012; Fantle and Higgins, 2014; Du Vivier et al., 2015; Griffith et al., 2015; Gussone et al., 2016; Lau et al., 2017; Higgins et al., 2018; Ahm et al., 2019; Wei et al., 2019; Wang et al., 2019; Wang et al., 2021; Kitch et al., 2021). Calcium is transferred into the oceans through continental weathering and hydrothermal fluid release and is removed primarily via carbonate precipitation and burial (De La Rocha and DePaolo, 2000). During carbonate precipitation, Ca is isotopically fractionated because the lighter ^{40}Ca or ^{42}Ca isotope is incorporated into the crystal lattice, leaving the residual seawater enriched in heavier ^{44}Ca (Fantle, 2010). As a result, seawater $\delta^{44/40}\text{Ca}$ can be affected by changing source inputs and/or changes in fractionation, which is dependent on the rate of carbonate precipitation and other environmental factors such as changes in temperature (Tang et al., 2008; Bohm et al., 2012). If the forcing is large enough it can be measured over short geologic time periods (<100 kyr) as was demonstrated with the Permo–Triassic and end Permian interval (Payne et al., 2010; cf. Komar and Zeebe, 2016; Wang et al., 2019). Because of coupling between the C and Ca cycles, inferred seawater $\delta^{44/40}\text{Ca}$ variation may elucidate changes in the Ca cycle and improve our understanding of the response of the C cycle to climatic perturbations (Urey, 1952; Walker et al., 1981; Berner et al., 1983).

As highlighted by previous studies, the interpretation of the marine $\delta^{44/40}\text{Ca}$ record is challenging for several reasons. Specifically, there is limited isotopic leverage between continental riverine inputs and hydrothermal inputs, Ca isotope fractionation during precipitation is highly variable, and Ca isotopes in carbonates are susceptible to resetting (e.g. De la Rocha and DePaolo, 2000; Gussone et al., 2003, 2005, 2006; Böhm et al., 2006, 2009; Sime et al., 2007; Farkaš et al.,

2007a, 2007b; Griffith et al., 2008; Fantle, 2010; Blättler et al., 2012, 2014; Holmden et al., 2012; Blättler and Higgins 2014; Fantle and Tipper, 2014; Jost et al., 2017; Lau et al., 2017; Higgins et al., 2018; Ahm et al., 2019). However, if forcing is large enough, observable variation in seawater $\delta^{44/40}\text{Ca}$ may occur. To date, two studies (Blättler et al., 2011 and Du Vivier et al., 2015) have been carried out to constrain the paleoclimate response of $\delta^{44/40}\text{Ca}$ during OAE 2 and both have divergent interpretations.

Blättler et al. (2011) examined $\delta^{44/42}\text{Ca}$ variation in 4 OAE 2 sections - Resolution Guyot (ODP site 866A); Eastbourne, England; Coppitella, Italy; and South Ferriby, England. A synchronous negative $\delta^{44/42}\text{Ca}$ excursion is present in all 4 sections, concurrent with the positive $\delta^{13}\text{C}$ excursion that marks the onset of OAE 2. This $\delta^{44/42}\text{Ca}$ excursion was interpreted to represent an increase in temperature and a threefold increase in continental weathering (Blättler et al., 2011). Additionally, the authors argued that increased weathering was coupled to high background levels of hydrothermal activity. The samples used in this study were from sections that were nearly pure carbonate with limited organic carbon, deposited in environments that were interpreted to be well-oxygenated (Eldrett et al., 2014). Although they express the global $\delta^{13}\text{C}$ excursion of the Cenomanian–Turonian boundary that marks OAE 2, changes in local water chemistry, such as anoxic/euxinic conditions, within which the carbonate is precipitating could have affected these isotopic values.

Du Vivier et al. (2015) generated a high-resolution $\delta^{44/40}\text{Ca}$ curve, for the WIS Portland core, and sections from Pont d'Issole France, Oyubari, Japan, and the Eastbourne, UK section analyzed by Blättler et al. (2011). The results significantly differ from the previously published records, including from the Eastbourne section. Three sections measured (except for the Oyubari Japan section) including the re-analysis of the Eastbourne, show a positive $\delta^{44/40}\text{Ca}$ excursion at

the start of OAE 2 while the Oyubari section shows a negative excursion. Discrepancies in the Eastbourne data were attributed by Du Vivier et al. (2015), who did the measurements via TIMS, to be the result of inter-laboratory bias as well as failure to account for measurement bias from the MC-ICPMS in the Blättler et al. (2011) study.

The positive $\delta^{44/40}\text{Ca}$ excursion was interpreted to represent a change in the Ca isotope fractionation factor, coincident with an increase in temperature (Du Vivier et al., 2015). The negative excursion of the Oyuburi section in Japan was interpreted to result from diagenetic alteration, erasing any potential seawater signal. Additionally, Du Vivier et al. (2015) hypothesized that a putative positive $\delta^{44/40}\text{Ca}$ excursion is missing from the South Ferriby section because of a large stratigraphic gap, concluding that the observed negative $\delta^{44/40}\text{Ca}$ excursion (Blättler et al., 2011) is not complete and instead records a change in fractionation factor, and the signal isn't reflective of seawater as it may have been altered.

This discrepancy of OAE 2 $\delta^{44/40}\text{Ca}$ records to date, necessitates an additional study from a different sedimentological record so that robust constraints on the $\delta^{44/40}\text{Ca}$ response can be ascertained. Laboratory studies have shown that stable Sr isotope ratios can help in the interpretation of calcium isotopes (Tang et al., 2008; Bohm et al., 2012). This is because, Ca and Sr have been shown to behave similarly during carbonate precipitation and isotope fractionation (e.g. Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Krabbenhöft et al., 2009, 2010; Böhm et al., 2012; Stevenson et al., 2014; Vollstaedt et al., 2014; Voigt et al., 2015; AlKhatib and Eisenhauer, 2017a,b; Andrews et al., 2016; Andrews and Jacobson, 2017; Wang et al., 2019; Shoa et al., 2020; Wang et al., 2020).

Hence, this study seeks to generate a new high-resolution $\delta^{44/40}\text{Ca}$ through OAE 2 from the Iona-1 core of the Western Interior seaway to understand the calcium isotope response during OAE

2. Also, the new record from Iona-1 would produce a more complete record of the OAE 2 response and it has recently been shown by Jones et al. (2020) that the onset of OAE 2 at the Portland core is marked by a 60 kyr hiatus. These new results combined with $\delta^{88/86}\text{Sr}$ data on the same samples will help in the interpretation of the $\delta^{44/40}\text{Ca}$ as well as elucidate the role of CaCO_3 precipitation to drive changes in $\delta^{44/40}\text{Ca}$ isotope values during this time. This is because Sr and Ca incorporation into the carbonate lattice have been shown to inversely correlate with precipitation rate (Bohm et al., 20212). Additionally, the results generated here will be compared with both in experimental (Tang et al., 2008; Böhm et al., 2012) and in natural settings (Wang et al., 2020; Wang et al., 2021) to test whether the $\delta^{44/40}\text{Ca}$ during OAE 2 was precipitation rate driven.

3.3 Geological setting

The Iona-1 core was drilled on a carbonate shelf at the southern gateway to the WIS in present-day southwest Texas (Fig. 3.1; 29°13.51'N, 100°44.49'W). The core recovered 180 m of Lower Cenomanian to Lower Coniacian marine sediment composed of marls and shales, with intermittent bentonite of the Boquillas Formation of the Eagle Ford Group (Eldrett et al., 2014). Sedimentation was slow and assumed to be relatively continuous during OAE 2 in the study setting (Eldrett et al., 2015a). An age model for the Iona-1 core was constructed from rhythmically deposited inter-bedded limestones and marlstones that were interpreted to reflect orbitally forced on sedimentation patterns and is supported by U-Pb zircon dating of bentonite beds (Eldrett et al. 2014, 2015a, 2015b; Minisini et al., 2017). The interbedded marls are predominantly finely laminated and C-rich in the lower Eagle Ford and become more bioturbated up the core (Eldrett et al., 2014). Stratigraphic patterns in the traces of burrowing organisms and the diversity of benthic foraminifera documented periods of alternating oxic to dysoxic and

anoxic bottom waters in the study area during OAE 2. Intervals of C-rich laminated sediment and elevated trace metal nutrients (U, Zn, Co, Ni, Cu, and Mo) are associated with bottom water anoxia (Eldrett et al., 2014; 2015a and Minisini et al., 2017). The depth of deposition is interpreted to be consistently below storm wave base in a restricted, sediment-starved setting (100 to 200m depth; Eldrett et al, 2014). A decrease in initial $^{187}\text{Os}/^{188}\text{Os}$ begins ~60 kyr before the onset of the positive CIE that traditionally marks the base on OAE 2 and, consistent with recently published Os isotope evidence supporting a volcanic trigger hypothesis for OAE 2 (DuVivier et al., 2014, Jones et al., 2020). The carbonate fraction of the sediment is mostly original low magnesium calcite mud derived from planktic foraminifera and calcispheres. Further details on the sedimentology, stratigraphy, and hydrographic conditions are in Eldrett et al., (2014, 2015a, 2017) and Minisini et al. (2017).

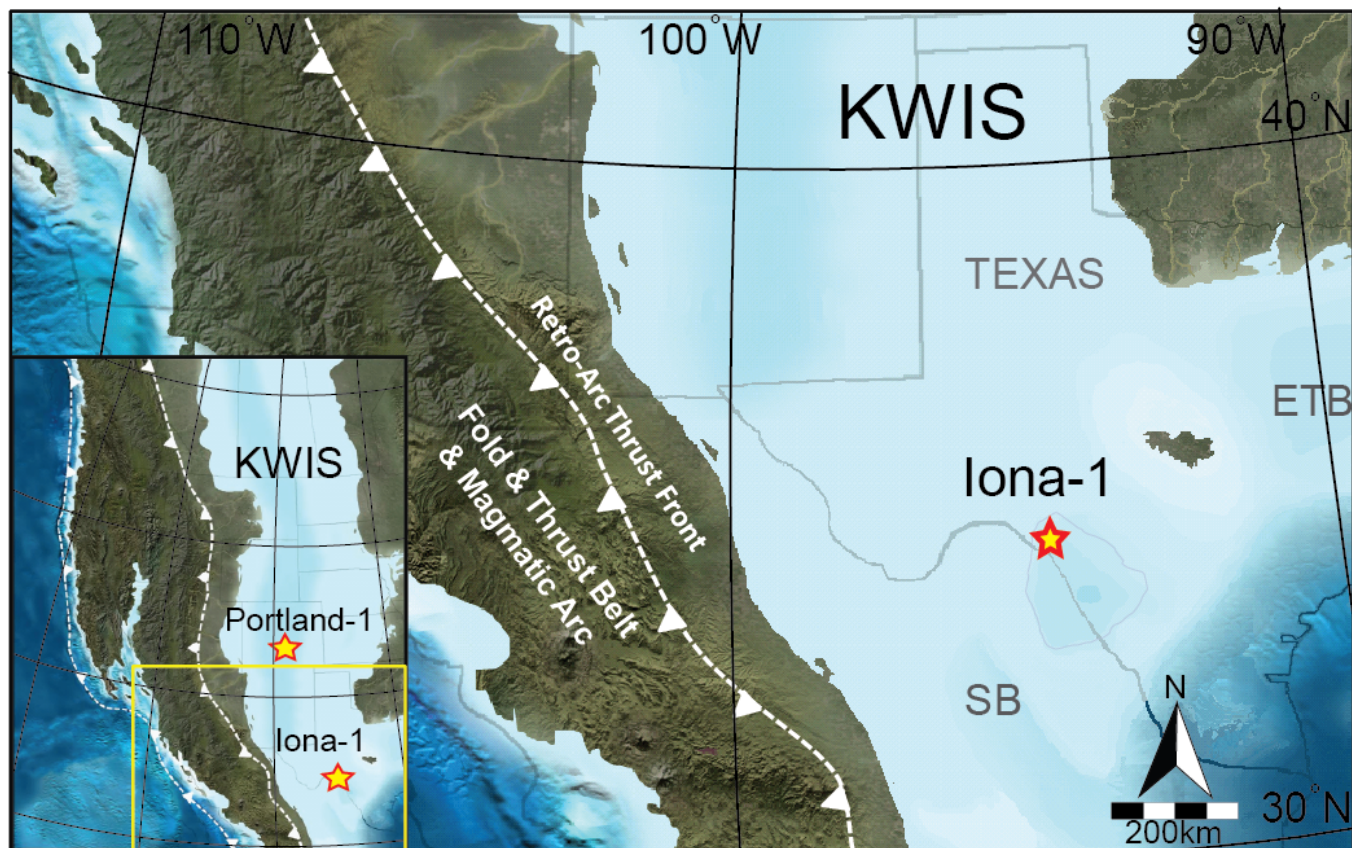


Figure 3.1: Early Turonian paleogeographic map showing the location of Shell Iona-1 and U.S. Geological Survey Portland-1 cores, modified from Eldrett et al., 2014. WIS—Cretaceous Western Interior Seaway.

3.4 Methods

3.4.1 Sample preparation and Elemental concentrations

The carbonate fractions of the Iona-1 core are employed to better understand the changes in ocean chemistry during OAE 2. Carbonates can precipitate directly from seawater, and thus may provide a record of the ocean conditions. The Iona-1 core samples are mixtures of fine-grained silicates, biogenic carbonate, and organic matter. A leaching technique was used to isolate the carbonate fractions for element and isotopic analysis. Multiple leaching methods, including sequential leaching or the employment of a weak acid, are to extract carbonates from silicate-bearing sedimentary rocks (Winter et al., 1995; Montanez et al., 1996; Bailey et al., 2000; Pietras et al., 2003; Li et al., 2011). In this study, the ammonium acetate leaching technique, which is well-established for carbonate and carbonate-rich rocks that do not have large allochems or skeletal material and similar to the samples from the Iona-1 core, was used (Montanez et al., 1996; Young et al., 2009; Edwards et al., 2015). Ammonium acetate treatment removes clay components through ion exchange, cleaning the target carbonate phases for dissolution. The remaining powder is then dissolved with 1M acetic acid, targeting the carbonate component without dissolution of silicate or organic components. Hence only the geochemistry of carbonate components is accessed with this technique. To verify this, trace element concentrations of the ammonium acetate leachates and extracted carbonates were obtained to screen for alteration and silicate contamination. Only samples with Sr/Mn ratios of > 2 , and low Rb/Sr (Montanez et al., 1996; Pietras et al., 2003) were further processed for Ca and Sr isotopic analysis. A proof of concept study was carried out using this method. Fifty milligrams of Iona-1 powdered samples were leached for 12 hours at 25°C in 1 ml of 1M ammonium acetate. This was followed by carbonate extraction in 1M acetic acid for 1 hour. Another set of the same samples were dissolved with a stronger acid (0.68N HNO₃) without

ammonium acetate treatment. Trace element concentrations were obtained using an Agilent QQQ ICPMS at the University of Houston.

Results for these tests are presented in Table 1. The ammonium acetate leach treatment can remove almost all of the Rb (highlighted in red in Table 1) from labile clay components which can significantly affect the results, especially for $^{87}\text{Sr}/^{86}\text{Sr}$ isotopes. Additionally, other clay-rich elements such as Al and Mg are elevated in both the ammonium acetate leachates and HNO_3 acid dissolutions but are not elevated in the acetic acid leachates, confirming that clay minerals were effectively removed in the acetate leachate. The degree of syn- and post-depositional diagenetic alteration can also be determined using Mn concentrations (Veizer, 1983). During the diagenetic fluid exchange with a reduced, Mn-enriched fluid, Mn is incorporated into the carbonate crystal lattice during recrystallization while Sr is removed during neomorphism to low-magnesian calcite (Veizer, 1983). Samples that have been diagenetically altered will typically have high Mn concentrations and low Sr/Mn ratios (Veizer, 1983; McArthur, 1994). The HNO_3 dissolutions show largely higher Mn concentrations because there was no pre-treatment of the samples with ammonium acetate. Thus, these experiments demonstrate that the developed leaching protocol used here can successfully target the trace element and isotopic analysis of the carbonate fractions in bulk shales.

Table 3.1: Trace element results in ppm for carbonate extraction proof of concept test.

	Sample #	Al	Ca	Mg	Sr	Mn	Rb	Sr/Mn	Rb/Sr
Ammonium Acetate leachate	1	3422.9	152993	3154.56	487.477	46.5668	8.88574	10.4683	0.01823
	2	2320.27	129985	5372.52	2551.35	25.8424	9.55567	98.7271	0.00375
	3	425.748	155850	4116.35	1714.41	138.777	10.0347	12.3537	0.00585
	4	1802.77	113382	3432.09	2082.02	21.2102	11.6354	98.1614	0.00559
	5	447.747	114433	2561.87	911.838	8.49818	8.03081	107.298	0.00881
Acetic acid leach	1	65.1744	125036	546.713	154.971	99.8986	0.08829	1.55128	0.00057
	2	114.442	147913	690.947	570.56	48.2466	0.16488	11.8259	0.00029
	3	87.7362	144009	812.22	382.233	324.686	0.09424	1.17724	0.00025
	4	132.886	141760	458.751	536.307	40.7409	0.14072	13.1638	0.00026
	5	107.309	156089	486.366	518.368	23.8843	0.13375	21.7033	0.00026
HNO3 Dissolution	1	396.483	337296	2027.07	488.365	221.863	0.48146	2.2012	0.00099
	2	826.647	346810	2728.06	1661.13	85.4334	1.22289	19.4436	0.00074
	3	347.668	373683	5162.15	1098.05	617.185	0.62379	1.77913	0.00057
	4	1004.88	371155	3661.48	1726.21	82.2641	1.3851	20.9838	0.0008
	5	569.59	376456	1697.18	1351.7	41.9823	1.10882	32.1969	0.00082

3.3.2 $^{87}\text{Sr}/^{86}\text{Sr}$, $^{88}/^{86}\text{Sr}$, and $^{44}/^{40}\text{Ca}$ Measurements via TIMS

Radiogenic and Stable Sr isotope ratios were measured using a Thermo Scientific Triton Plus thermal ionization mass spectrometer (TIMS) at the University of Houston using a multi-static measurement technique adapted from a method for obtaining high precision Nd isotopic ratios (Bennett et al., 2007). Nana Yobo et al. (2021) recently reviewed the method used for measuring $^{87}\text{Sr}/^{86}\text{Sr}$. In brief, the radiogenic Sr cuts were measured in a multi-static mode and instrumental mass fractionation was corrected by normalizing $^{88}\text{Sr}/^{86}\text{Sr}$ ratios to a value of 8.3752 using an exponential law.

An optimized ^{87}Sr - ^{84}Sr double-spike technique was used to measure $^{88}\text{Sr}/^{86}\text{Sr}$ ratios by TIMS at the University of Houston. To apply the double spike method (Rudge et al., 2009), 300ng of Sr from a stock solution was placed in a clean Teflon vial and spiked with the ^{87}Sr - ^{84}Sr double spike solution resulting in a sample spike mixture of 1.0. Once the solutions were added, the vials were closed and placed on a hotplate at 70°C for 2 hours to ensure complete sample-spike equilibration. Thereafter, the Sr fraction for each sample was purified from the sample matrix using Sr-Spec resin following methods described in Nana Yobo et al. (2021).

The purified fractions were then taken and loaded onto a single rhenium filament with TaF₅ solution. For each batch of TIMS analyses, spiked and unspiked samples of SRM987 were run in parallel (one at the beginning and one at the end) Also, to SRM987, the IAPSO seawater standard was also analyzed with each batch to verify the accepted values as a secondary and independent check. In the mass-spectrometer, a 6 V ^{88}Sr ion-beam was achieved before collecting data in a three-line multi-static mode for before collecting $^{88}\text{Sr}/^{84}\text{Sr}$, $^{87}\text{Sr}/^{84}\text{Sr}$, and $^{86}\text{Sr}/^{84}\text{Sr}$ ratios for 140 duty cycles having a 16 s integration time. Measurements were made with amplifier rotation to cancel out cup and electronic bias. The ^{85}Rb beam was monitored to confirm that ^{87}Rb

did not isobarically interfere with ^{87}Sr . The total analysis time was 1.5–2 hr per sample. Data were reduced using the Eugster et al. (1969) equations. Runs were carefully monitored to ensure a steady or increasing ^{88}Sr beam, an increasing $^{86}\text{Sr}/^{84}\text{Sr}$ fractionation pattern with time in the run, and the absence of reverse fractionation in both raw and fractionation-corrected ratios. The $^{88}\text{Sr}/^{86}\text{Sr}$ ratios are reported in δ notation relative to NBS 987 strontium carbonate standard, where

$$\delta^{88/86}\text{Sr} = [(^{88}\text{Sr}/^{86}\text{Sr})_{\text{sample}} / (^{88}\text{Sr}/^{86}\text{Sr})_{\text{NBS987}} - 1] \times 10^4$$

During the period of the study, repeated analysis yielded $\delta^{88/86}\text{Sr}_{\text{SRM987}} = 0.000 \pm 0.005\text{‰}$ (2σ , $n = 21$) and $\delta^{88/86}\text{Sr}_{\text{IAPSO}} = 0.397 \pm 0.004\text{‰}$ (2σ , $n = 21$). The external precision for $^{87}\text{Sr}/^{86}\text{Sr}$ is ± 5 ppm (2σ) based on repeated measurements of the SRM 987 standard yielding $0.710251 \pm 2.951\text{E-}06$ ($n=42$). The $^{88}\text{Sr}/^{86}\text{Sr}$ ratios data reduction includes the input of corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios first measured. The data reduction procedural blanks determined with an ^{84}Sr isotope dilution method were negligible compared to the amounts of Sr employed for both analyses (300 ng for $^{87}\text{Sr}/^{86}\text{Sr}$ and 300 ng for $^{88}\text{Sr}/^{86}\text{Sr}$).

Calcium isotope ratios ($^{44}\text{Ca}/^{40}\text{Ca}$) were measured using an optimized ^{43}Ca – ^{42}Ca double-spike following the TIMS technique described in Holmden et al. (2012) and modified by Lehn et al. (2013) at the Saskatchewan Isotope Laboratory at the University of Saskatchewan using a Thermo Fisher Triton TIMS. In summary, aliquots of 50 μg of Ca were mixed in clean Teflon vials with aliquots of ^{43}Ca – ^{42}Ca double spike to achieve a target mixed $^{40}\text{Ca}/^{42}\text{Ca}$ ratio of 7.0. After mixing, the solutions were capped and then set on a hot plate for 2 hours to allow for sample-spike equilibration. The solutions were then dried down, resolubilized, and dried down again to further promote equilibration of spike and sample isotopes. Using Savillex Teflon columns filled with 3 ml of Biorad MP50 cation exchange resin, Ca was purified from K. After the extraction, the purified Ca solutions were dried down on a hot plate at 60°C. After drying, two drops of H_2O_2 were

added and dried to help oxidize organics contributed from the column, followed by 2 drops of 15N HNO₃ to convert the samples to the nitrate form before loading.

An aliquot of 10–16µg of Ca is loaded onto a single Ta filament between paraffin dams, and 0.5 mg of 10% H₃PO₄ is added before analyses with TIMS. In the TIMS, the filament current was increased slowly until a 50V ⁴⁰Ca ion beam was achieved before collecting 180 sets of ⁴⁰Ca/⁴²Ca, ⁴²Ca/⁴³Ca, and ⁴²Ca/⁴⁴Ca ratios using a 3-hop duty cycle having variable integration times with total run times of about 3 hours per sample. Routine monitoring of the K beams demonstrated that no correction was needed for ⁴⁰K interference on ⁴⁰Ca. Cup and amplifier bias were reduced using amplifier rotation. An iterative procedure was used to correct instrumental mass fractionation and subtract the spike composition from the measured composition of the spike-sample mixture using equations published in Eugster et al. (1969). All results are reported in δ-notation relative to the OSIL Atlantic Seawater standard,

where $\delta^{44/40}\text{Ca}(\text{‰}) = [({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{smp}} / ({}^{44}\text{Ca}/{}^{40}\text{Ca})_{\text{sw}} - 1] \times 1000$.

The typical external precision of the $\delta^{44/40}\text{Ca}$ values is better than $\pm 0.05\text{‰}$ (2σ) and the long-term reproducibility of SRM 915b (NIST) standard is $-1.86 \pm 0.03\text{‰}$ (2σ).

3.5 Results

3.5.1 $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ isotope results

The $\delta^{44/40}\text{Ca}$ of the Iona-1 core varies from -1.63 ± 0.02 to $-1.29 \pm 0.03 \text{‰}$ ($\pm 2\text{se}$) and reproduces a positive excursion through OAE 2 (Fig. 3.2 and listed in Table 3.2). Importantly, the Iona-1 core data shows a complete $\delta^{44/40}\text{Ca}$ profile that is not previously recorded around the

onset of OAE 2 at the other WIS site represented by the Portland core (Figs. 3.1 and 3.3). This highlights the utility of this new sample set to produce complete records through the OAE 2 interval. In detail, before OAE 2 (120 – 115 m) the $\delta^{44/40}\text{Ca}$ at Iona begins around -1.46‰ and gradually decreases to about -1.62‰. Around the onset of OAE 2 (110.5 m) the $\delta^{44/40}\text{Ca}$ increases from -1.62‰ to -1.44‰ at 106 m. This is followed by a period of relatively unchanging $\delta^{44/40}\text{Ca}$ (105 – 103 m) After which point (103 – 80 m), the $\delta^{44/40}\text{Ca}$ values start to slowly decrease until the termination of OAE 2. The Iona-1 $\delta^{44/40}\text{Ca}$ record is punctuated by intervals of low $\delta^{44/40}\text{Ca}$. As stated above, the Iona-1 data is in close agreement with the Portland data except for the fact that the Iona-1 record fills in gaps that are missing not captured by the Portland core (~94.7 Ma; Fig. 3.3). Another striking similarity between the two values $\delta^{44/40}\text{Ca}$ values ~ - 1.3‰ at 103.44 and 104.14 which is also recorded in Portland core (red circle; Fig 3.3). However, the Iona-1 $\delta^{44/40}\text{Ca}$ data shows a lot more scatter before the onset of the event than during and after the event compared to the Portland record (Fig. 3.3).

The Iona-1 $\delta^{88/86}\text{Sr}$ profile, in general, shows a trend of increasing $\delta^{88/86}\text{Sr}$ towards the onset of OAE 2 and then decrease through OAE 2 until its termination. In detail, the $\delta^{88/86}\text{Sr}$ value beginning at 115 m show an increase from 0.22‰ to 0.29‰ at about 110 m. At 1109 – 90 m, the $\delta^{88/86}\text{Sr}$ values begin to decrease slowly from 0.29‰ back to 0.22‰. The $^{87}\text{Sr}/^{86}\text{Sr}$ (Nana Yobo et al., 2021) shows an increasing trend in $^{87}\text{Sr}/^{86}\text{Sr}$ before the onset of OAE 2 (130 – 113 m) followed by a decreasing trend in the early part of OAE 2 (113 – 105 m), a period of no change in $^{87}\text{Sr}/^{86}\text{Sr}$ in the middle part of OAE 2 (105 – 100 m), and a resumption of the declining trend in $^{87}\text{Sr}/^{86}\text{Sr}$ for the remainder of OAE 2 and beyond (100 – 80 m). The shift to decreasing trend in $^{87}\text{Sr}/^{86}\text{Sr}$ occurs at the same interval (113 m) as the decrease in $^{187}\text{Os}/^{188}\text{Os}$ ratios signaling the massive increase in LIP volcanism. The ~ 150 kyr of no change in $^{87}\text{Sr}/^{86}\text{Sr}$ occurs

in a stratigraphic interval marked by the beginning of the post-volcanic rise in oceanic $^{187}\text{Os}/^{188}\text{Os}$ ratios, and the end of the peak positive shift in sedimentary $\delta^{13}\text{C}$ values

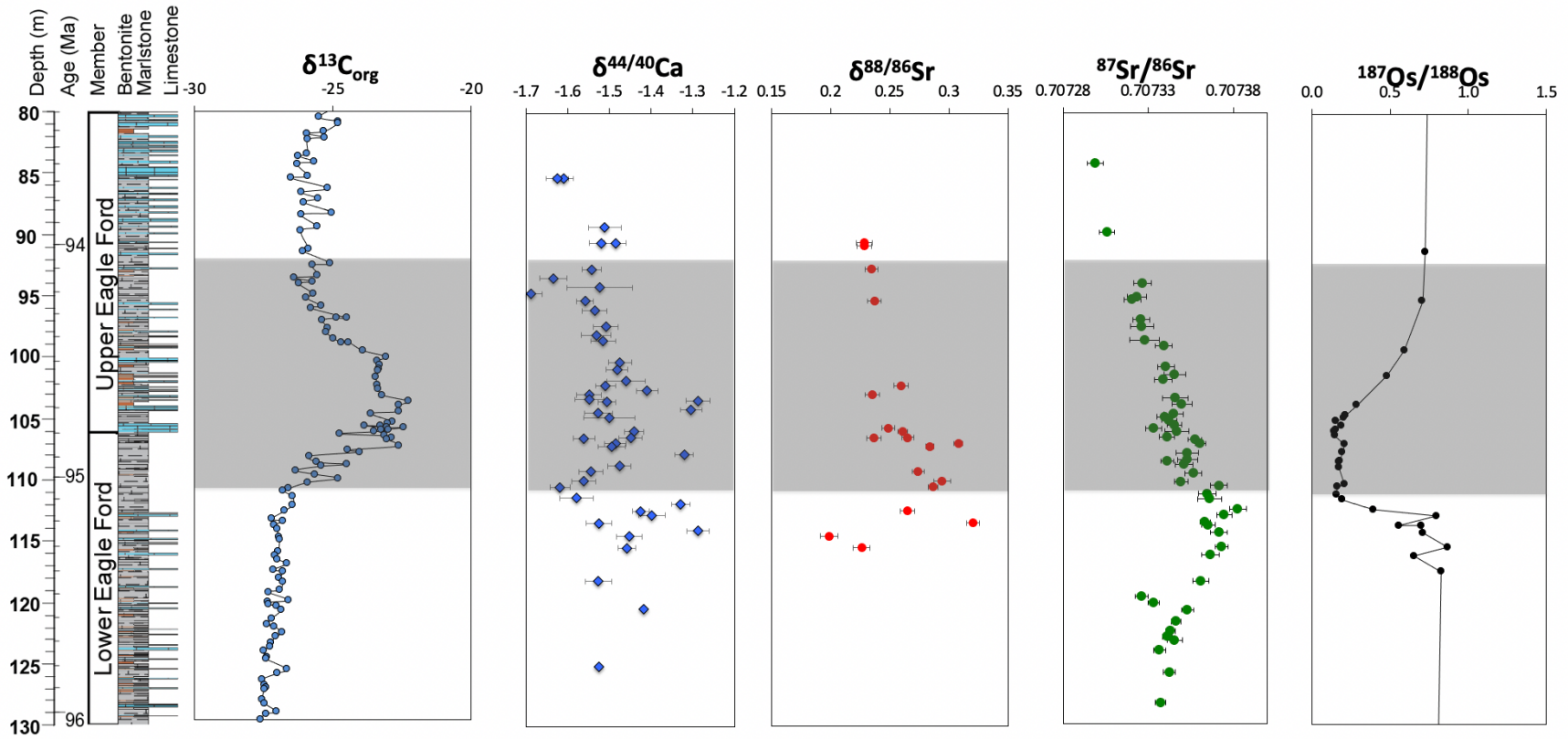


Figure 3.2: Stratigraphic correlation of OAE 2 record from the Iona-1 core $\delta^{13}\text{C}_{\text{org}}$ (A: Eldrett et al., 2014), $\delta^{44/40}\text{Ca}$ (B) $\delta^{88/86}\text{Sr}$ (C), $^{87}\text{Sr}/^{86}\text{Sr}$ (D; from Nana Yobo et al., 2021), $^{187}\text{Os}/^{188}\text{Os}$ (E; from Sullivan et al., 2020). The OAE 2 interval is shaded in gray based on shifts to more positive $\delta^{13}\text{C}_{\text{org}}$ (Modified from Eldrett et al., 2014). Error bars represent $\pm 2\text{SE}$ uncertainty.

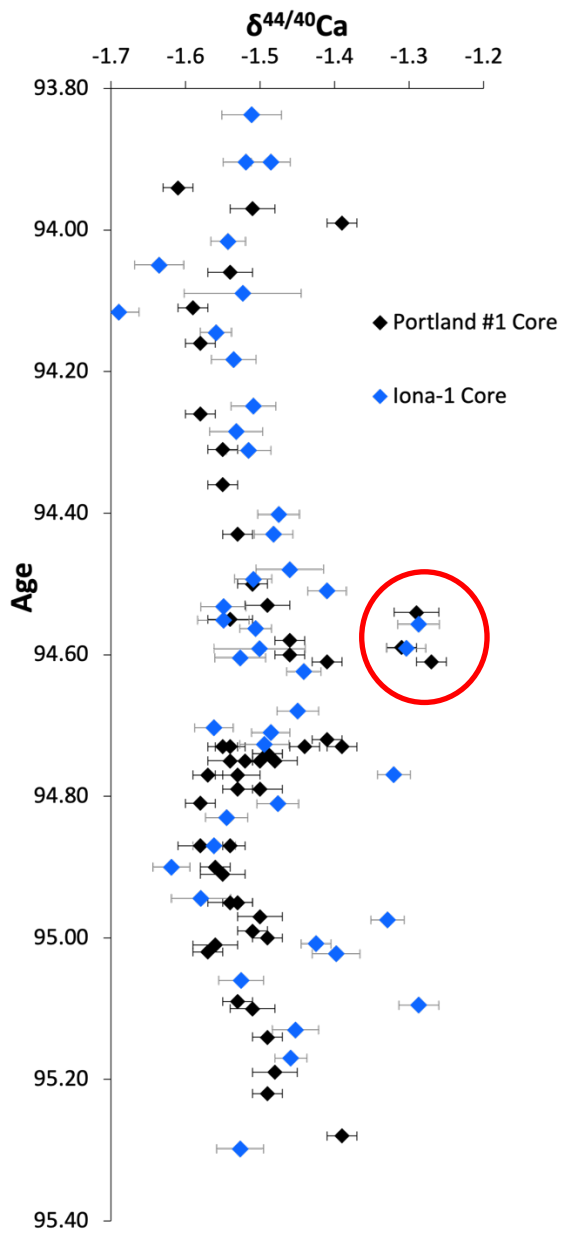


Figure 3.3: Stratigraphic correlation of $\delta^{44/40}\text{Ca}$ between the Portland and Iona-1 core. $\delta^{44/40}\text{Ca}$ Portland data from Du Vivier et al., (2015) and $\delta^{44/40}\text{Ca}$ Iona-1 from this study

Table 3.2: $\delta^{44/40}\text{Ca}$, $\delta^{88/86}\text{Sr}$, and $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ (calcite and organic) and TOC of the Iona-1 core

Stratigraphic height (m)	$\delta^{44/40}\text{Ca}$ (sw)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{88/86}\text{Sr}$	$\delta^{13}\text{C}$ calcite	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$ org	TOC (Wt %)
80.25		0.707299		0.47	-5.20	-25.65	0.53
85.31	-1.63	0.707306		1.86	-6.27	-26.14	3.31
89.32	-1.51	0.707327		0.82	-5.65	-25.72	1.04
90.57	-1.52	0.707323	0.228	0.40	-5.45	-25.70	0.99
90.83		0.707321	0.228				
92.73	-1.54	0.707326	0.234	1.45	-5.79	-24.48	0.92
93.44	-1.64	0.707326		2.06	-6.33	-25.36	3.87
94.22	-1.52			1.97	-6.16	-25.22	2.70
94.73	-1.69	0.707328		2.20	-5.93	-24.97	1.87
95.32	-1.56	0.707339	0.237	2.52	-6.12	-24.41	4.33
96.10	-1.54			2.76	-5.63	-23.30	1.43
97.41	-1.51	0.707340		2.81	-6.00	-23.34	6.84
98.08	-1.53	0.707346		2.69	-5.79	-23.44	2.08
98.56	-1.52	0.707339		2.64	-5.85	-23.20	1.35
100.30	-1.48	0.707346		2.80	-5.76	-22.26	4.87
100.90	-1.48	0.707350		1.82	-6.25	-22.61	2.58
101.83	-1.46	0.707345	0.293	2.11	-7.01	-23.61	1.91
102.21	-1.51	0.707340					
102.63	-1.41	0.707342	0.299	3.75	-5.50	-22.82	1.45
102.95	-1.55	0.707345		3.75	-5.50	-22.76	1.30
103.33	-1.55	0.707333	0.291	1.61	-5.14	-23.83	2.50
103.44				-1.09	-5.31	-23.03	0.93

103.54	-1.51	0.707347		2.26	-4.95	-22.42	0.65
104.18		0.707341		0.58	-5.37	-24.74	0.27
104.44	-1.53	0.707357	0.280	3.41	-5.58	-23.12	2.47
104.83	-1.50	0.707361		3.15	-5.84	-23.02	2.48
105.68		0.707353	0.249	1.90	-5.56	-24.44	0.90
105.96	-1.44		0.261	0.71	-5.39	-24.01	0.62
106.45	-1.45	0.707353	0.265	1.61	-6.57	-25.84	2.66
106.50	-1.56	0.707341	0.236	1.43	-6.44	-25.56	2.17
106.94	-1.49	0.707351	0.308	1.65	-5.33	-24.47	1.59
107.17	-1.49		0.284	1.58	-6.51	-26.32	3.73
107.82		0.707356		1.90	-6.08	-24.78	5.11
108.77	-1.48	0.707349		1.24	-6.30	-25.90	3.05
109.22	-1.54	0.707371	0.274	0.96	-6.53	-26.79	6.04
110.01	-1.56	0.707365	0.294	1.44	-6.51	-26.44	3.34
110.49		0.707366	0.287	1.46	-6.36	-26.43	4.71
111.36	-1.58	0.707383		0.41	-5.82	-26.73	4.79
111.88		0.707375	0.256	1.15	-6.51	-27.19	3.65
112.45	-1.42	0.707363	0.265	0.99	-6.70	-26.79	3.65
112.77	-1.40	0.707365	0.268	1.11	-6.30	-27.00	5.26
113.42	-1.53	0.707372	0.318	2.08	-5.27	-26.94	1.23
114.04			0.227	0.91	-6.62	-26.91	5.41
114.50	-1.45	0.707373	0.201	1.22	-6.24	-26.95	6.98
115.45	-1.46	0.707367	0.226	1.43	-6.72	-26.92	4.08
118.16	-1.53	0.707361	0.294	1.19	-6.68	-27.32	7.92
119.77		0.707326		2.00	-5.70	-26.58	1.20
120.40	-1.42	0.707333	0.295	1.69	-6.69	-27.03	8.23
121.09		0.707353	0.296	1.52	-7.27	-27.19	4.60
122.18		0.707346	0.313	1.52	-6.70	-27.10	7.21

123.14		0.707343	0.358	-3.79	-3.32	-26.82	0.61
123.68		0.707341	0.315	1.25	-6.60	-27.04	7.28
124.03		0.707345	0.331	1.12	-7.10	-27.25	4.90
125.13	-1.53	0.707337		1.06	-6.81	-26.64	9.87
127.31		0.707342	0.370	0.72	-6.46	-27.46	8.85
129.27				2.04	-5.33	-27.54	1.31
130.17		0.707337			-2.91	-27.49	1.41
135.25		0.707362		0.07	-6.52	-27.14	11.59

3.5.2 Elemental and isotopic cross plots

The isotopic values ($\delta^{88/86}\text{Sr}$, $\delta^{44/40}\text{Ca}$) as well as the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are plotted against each other and various elemental concentrations and ratios (Mg/Ca, Sr/Ca, and Mn/Sr ratios and [Sr]) as well as the calculated CaCO_3 (wt%) assuming stoichiometric CaCO_3 . The cross plots are plotted using standardized major axis (SMA) regression model to evaluate any statistical significance or correlation. The SMA model is ideal because both x and y variables are independent variable. While, the SMA regression statistics shows a significant relationship between the values, the strength of the correlation across the various parameters is very weak (Fig. 3.4 & 3.5, values listed in Table 3.3).

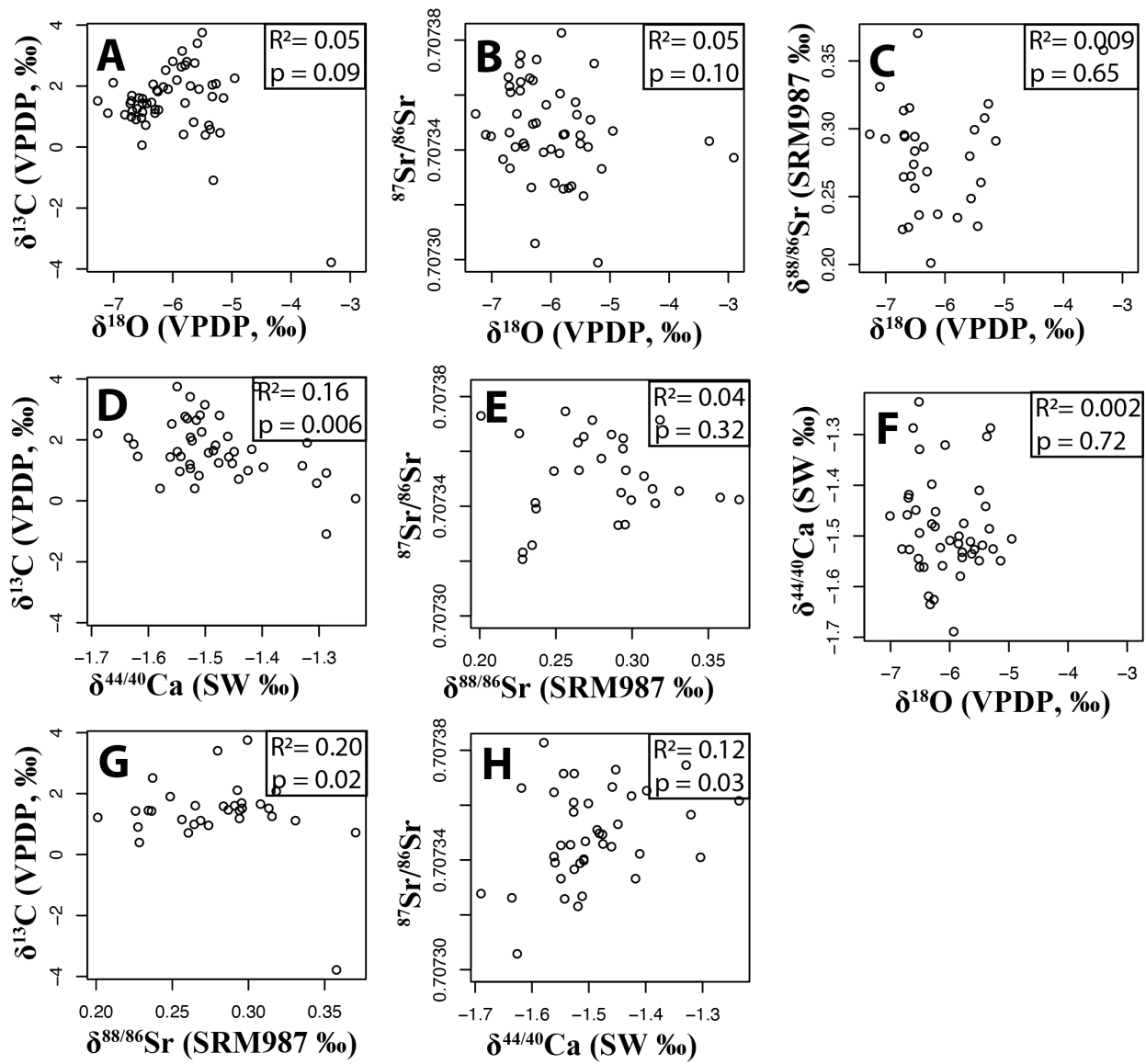


Figure 3.4: Cross plot of various isotope ratios of the carbonate fraction from the Iona-1 core.

(A) $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}_{\text{calcite}}$, (B) $\delta^{18}\text{O}$ vs $\delta^{88/86}\text{Sr}$, (C) $\delta^{44/40}\text{Ca}$ vs $\delta^{88/86}\text{Sr}$, (D) $\delta^{44/40}\text{Ca}$ vs $\delta^{13}\text{C}_{\text{calcite}}$ (E)

$\delta^{18}\text{O}$ vs $^{87}\text{Sr}/^{86}\text{Sr}$ (F) $\delta^{88/86}\text{Sr}$ vs $^{87}\text{Sr}/^{86}\text{Sr}$, (G) $\delta^{88/86}\text{Sr}$ vs $\delta^{13}\text{C}_{\text{calcite}}$, (H) $\delta^{18}\text{O}$ vs $\delta^{44/40}\text{Ca}$ and (I)

$\delta^{44/40}\text{Ca}$ vs $^{87}\text{Sr}/^{86}\text{Sr}$. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from Eldrett et al., 2015a

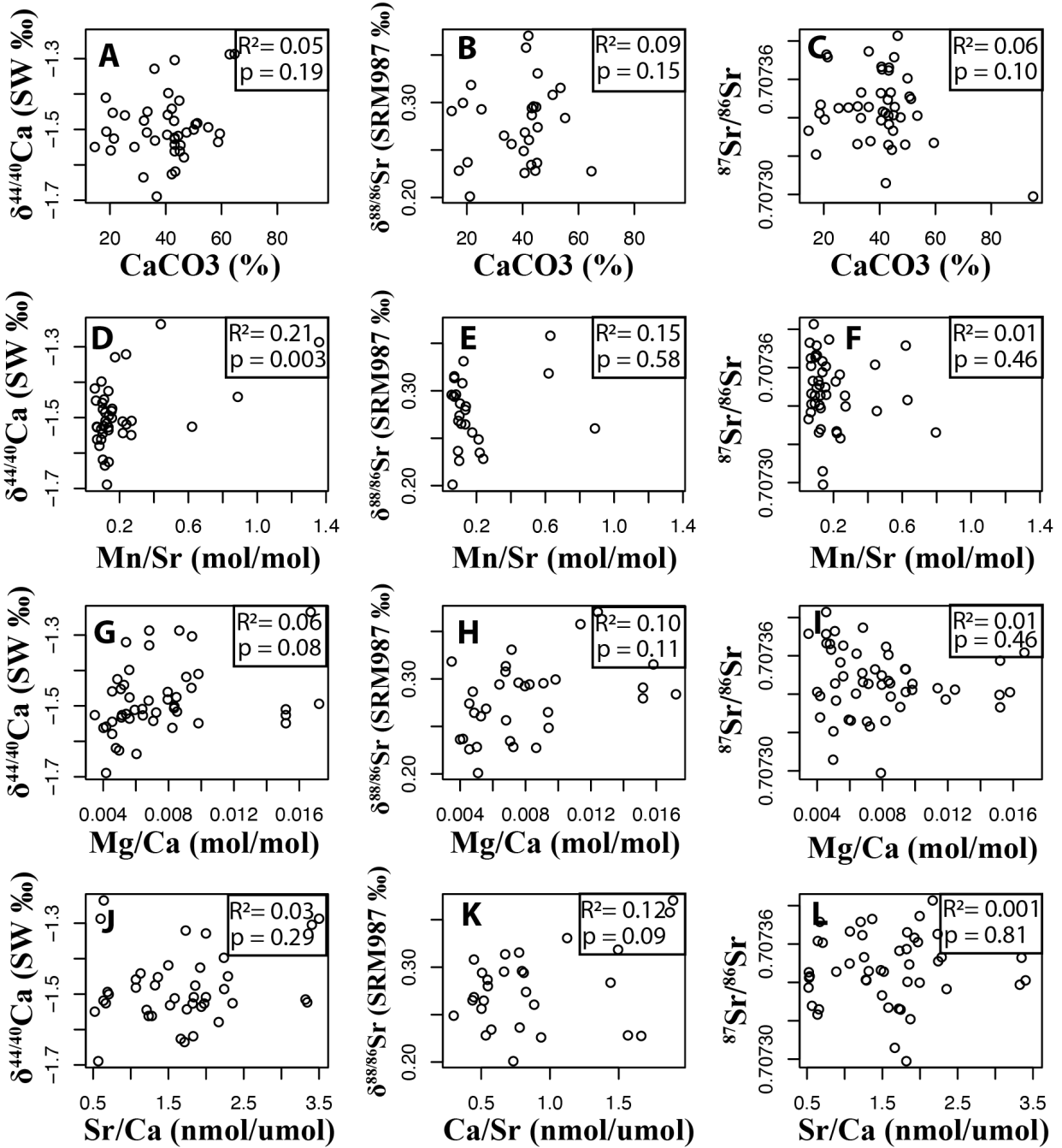


Figure 3.5: Cross plot of various isotope and elemental of the carbonate fraction from the Iona-1 core. (A) $\delta^{44/40}\text{Ca}$ vs CaCO_3 (B) $\delta^{88/86}\text{Sr}$ vs CaCO_3 , (C) $^{87}\text{Sr}/^{86}\text{Sr}$ vs CaCO_3 (D) $\delta^{44/40}\text{Ca}$ vs Mn/Sr (E) $\delta^{88/86}\text{Sr}$ vs Mn/Sr (F) $^{87}\text{Sr}/^{86}\text{Sr}$ vs Mn/Sr , (G) $\delta^{44/40}\text{Ca}$ vs Mg/Ca , (H) $\delta^{88/86}\text{Sr}$ vs Mg/Ca , (I) $^{87}\text{Sr}/^{86}\text{Sr}$ vs Mg/Ca , (J) $\delta^{44/40}\text{Ca}$ vs Sr/Ca , (K) $\delta^{88/86}\text{Sr}$ vs Ca/Sr and (L) $^{87}\text{Sr}/^{86}\text{Sr}$ vs Sr/Ca .

Table 3.3: Elemental concentration of carbonate fraction from the Iona-1 Core

Stratigraphic height (m)	Carbonate wt %	Al (ppm)	Mn (ppm)	Rb (ppm)	Sr (ppm)	Ca (ppm)	Mg (ppm)
80.25	95	183	47	0.29	543	136622	647
85.31	42	165	52	0.29	603	165759	494
89.32	59	235	123	0.42	898	259443	922
90.57	44	164	65	0.30	433	310031	1344
90.83	17	35			1242	303029	909
92.73	43	137	39	0.20	284	74539	315
93.44	32	163	29	0.21	401	106882	387
94.22	43	131	57	0.26	845	115681	373
94.73	37	156	32	0.29	403	325388	813
95.32	20					325388	813
96.10	59	141	41	0.20	483	114117	383
97.41	47	134	35	0.20	470	117066	447
98.08	36	173	33	0.23	563	169223	517
98.56	41	124	53	0.20	666	91667	467
100.30	32	138	37	0.17	374	129627	657
100.90	51	90	63	0.40	659	282063	1343
101.83	25					282063	1343
102.21	33	218	37	0.21	219	50203	456
102.63	19					229790	1352
102.95	29	163	44	0.18	263	229790	1352
103.33	15					212754	1934
103.44	63	120	403	0.10	473	61793	252

103.54	19					232708	1164
104.18	43				1072	144009	812
104.44		88	72	0.46	848	212754	1934
104.83	50	230	35	0.32	360	232708	1164
105.68	40	413	141	0.42	1055	144009	812
105.96	42	247	360	0.33	647	262237	828
106.45	33	170	33	0.26	474	94654	532
106.50	45	487	55	0.57	945	337639	810
106.94	51	218	42	0.28	568	115934	470
107.17	55	178	41	0.31	472	311186	3206
107.82		133	80	0.30	536	141760	459
108.77	43	142	31	0.22	483	119026	399
109.22	45	334	49	0.31	768	290291	792
110.01	43	415	33	0.54	765	283132	1395
110.49	43	179	77	0.36	1179	294517	842
111.36	47	141	38	0.32	718	151460	413
111.88	36	224	77	0.56	704	161165	657
112.45		110	61	0.25	720	171153	498
112.77	41	161	35	0.34	588	120380	403
113.42	21	73	183	0.28	471	321877	671
114.04	65			0.071	284	216687	1122
114.50	21	344	37	0.44	956	320749	976
115.45	41	162	48	0.39	771	329831	900
118.16		248	37	0.21	837	194023	745
119.77	49	126	221	0.21	443	308082	1511
120.40	45	260	29	0.24	827	252370	1373
121.09	44	230	42	0.19	831	302229	1368
122.18		617	48	0.56	1081	333626	1359

123.14	41	94	150	0.05	380	325393	2214
123.68	54	373	38	0.38	840	298014	2820
124.03	45	100	44	0.16	566	291448	1246
125.13	43	434	37	0.47	865	168105	519
127.31	42	111	20	0.25	345	299327	2227
129.27						105251	661
130.17		101	102	0.09	360	315696	2243
135.25		40	95	0.09	344	245300	2450

3.6 Discussion

Before interpreting the data, it is important to consider whether the $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ signals recorded here are primary and or may have been affected by diagenetic alteration. This is because diagenetic alteration early or late has been shown to affect the isotopic composition of bulk carbonates (Brand and Veizer, 1980).

3.6.1 Diagenesis

A cross plot between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Fig. 3.4A) shows no correlation ($R^2 = 0.05$). This supports the absence of any significant diagenetic alteration post lithification. However, the similarity between the Iona-1 and Portland records even with the three high points of Portland (red circle Fig. 3.3) which were interpreted by Du Vivier et al. (2015) to likely be a result of diagenesis, suggest that whatever is creating this effect is not late diagenesis. This is because late diagenetic alteration would likely not be manifested equally in two different locales more than 2000 km apart. In addition to these two points that are present in both Iona-1 and Portland records, the Iona-1 record also exhibits other intervals of relatively high $\delta^{44/40}\text{Ca}$ (114.14, 112.77, 112.45 111.88, and 107.82 m depth respectively). These intervals of elevated $\delta^{44/40}\text{Ca}$ are herein interpreted to have resulted from syn-depositional diagenesis. Syn-depositional diagenesis is an early diagenesis process, where the sediment is being altered before lithification (Bathurst, 1972; Flugel, 2013) and occurs in two ways; recrystallization or neomorphism. Recrystallization involves the dissolution and re-precipitation of new calcite material from existing crystals, while neomorphism has to do with the *in-situ* transformation of aragonite to calcite (e.g., Folk, 1965; Flügel, 2013; Lau et al., 2017; Higgins et al., 2018).

Syn-depositional diagenesis is especially common in platform carbonates and has been shown to elevate the $\delta^{44/40}\text{Ca}$ values (Higgins et al., 2018). Additionally, the interval of elevated $\delta^{44/40}\text{Ca}$ also corresponds with the interval of elevated ^{192}Os abundances (Fig. 3.6). This likely indicates that there was an increased flux of Os into the depositional environment through upwelling and that upwelling carried CO_2 -rich waters that were corrosive to carbonates deposition. Hence, syn-depositional diagenesis, in the Iona-1 core was through submarine dissolution-recrystallization events. Recrystallization in the presence of seawater would drive $\delta^{44/40}\text{Ca}$ isotopes heavy (towards seawater value) due to the incorporation of seawater Ca with little to no fractionation occurring (Fantle and DePaolo 2007). Except for these seven data points that have elevated $\delta^{44/40}\text{Ca}$ hovering around -1.3‰, the close similarity of the $\delta^{44/40}\text{Ca}$ with that of Portland data suggest that the rest of the Iona-1 Ca isotope signal is primary.

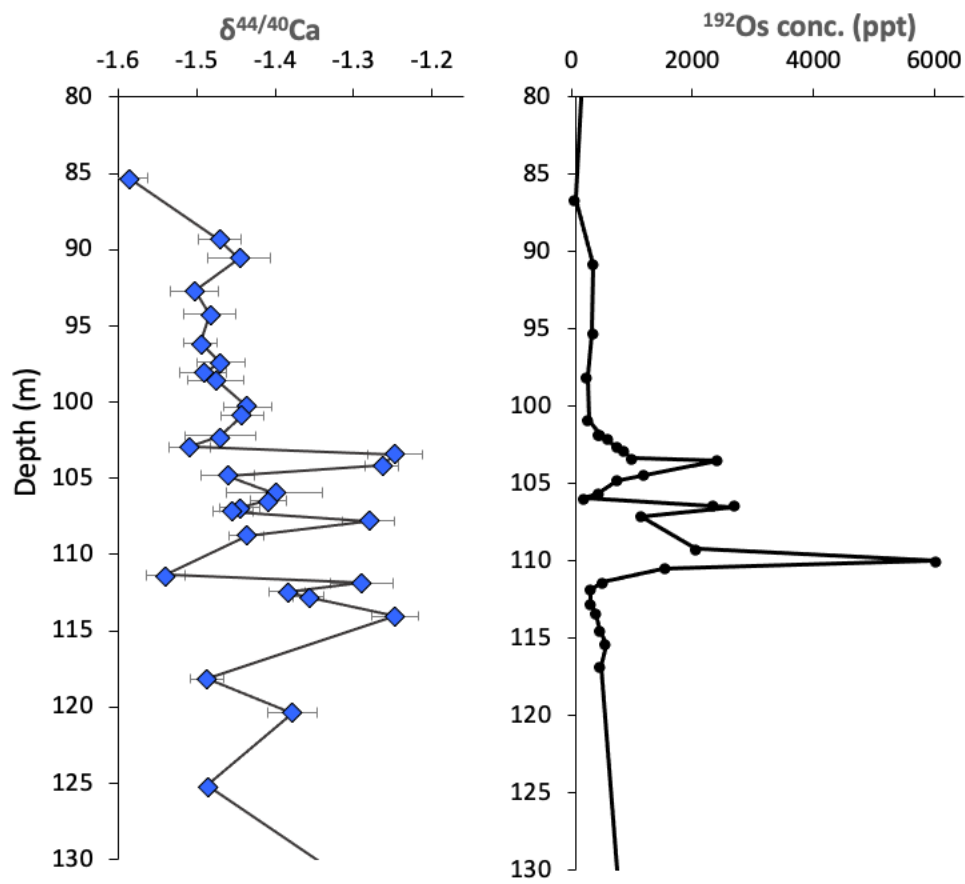


Figure 3.6: Stratigraphic correlation, showing the relationship between $\delta^{44/40}\text{Ca}$ and Os concentrations of the Iona-1 core. Os data from Sullivan et al., 2020.

Further discussion on diagenetic effect was can be found above in section 1.6.1. Additionally, Figs. 3.4 and 3.5 show cross plots of various parameters to evaluate any statistical significance and apparent correlations within the data. In these plots, there is no strong statistical correlations exist between these various parameters.

3.6.2 Comparison of the $\delta^{44/40}\text{Ca}$ with the Portland Core

There currently exists a discrepancy of what the Ca isotope response is during OAE 2. Blättler et al. (2011) reported a negative excursion, while DuVivier et al. (2015) reported a positive excursion. The difference in the response has been attributed to instrumentation technique. The data for Iona-1 carbonates were measured on a Triton TIMS at the Saskatchewan Isotope Laboratory at the University of Saskatchewan, Saskatoon, Canada. The $\delta^{44/40}\text{Ca}$ results (Fig. 3.3) vary from -1.63 ± 0.02 to -1.29 ± 0.03 ‰ ($\pm 2\text{se}$) and reproduce the positive excursion reported by DuVivier et al. (2015) for the Portland core. Given the similarity between the Iona-1 and Portland data, indicates that the calcium isotope response during OAE 2 is likely a positive excursion. However, the Iona-1 data except for two data points at 108.18 and 103.44 m, show more variation below the OAE 2 interval with some elevated $\delta^{44/40}\text{Ca}$ as opposed to the steady ‘background’ values recorded in the Portland #1 core.

3.6.3 Chemical Weathering

Early study (Blättler et al., 2011) of Ca isotope response through OAE 2 section attributes the response of calcium isotopes as a function of significant weathering increase. This

was further supported by subsequent studies of $\delta^{17}\text{Li}$ isotopes (Pogge von Strandmann et al., 2013). However, the positive excursion in $\delta^{44/40}\text{Ca}$ by DuVivier et al., (2015) and the new data presented here, challenges this notion, because the response cannot be interpreted to have resulted from weathering as there is no isotopic leverage in the $\sim 0.2\text{‰}$ variation of $\delta^{44/40}\text{Ca}$ recorded during OAE 2. This is because the $\delta^{44/40}\text{Ca}$ isotopic composition of continental weathering and the hydrothermal ratio is very close (-1.03‰ and -0.95‰ respectively; Holmden et al., 2012). Thus to account for such a change by weathering means a huge increase in the weathering flux into the ocean. Additionally, a recent study using Sr isotopes (Nana Yobo et al., 2021) also was not consistent with the 3-fold increase in weathering previously reported during this interval. Hence the $\delta^{44/40}\text{Ca}$ variation during OAE 2 cannot be interpreted based on chemical weathering.

There are two other possibilities for what could have driven the change in $\delta^{44/40}\text{Ca}$ before and during OAE 2. One possibility is a change in CaCO_3 mineralogy. An increase in $\delta^{44/40}\text{Ca}$ could result from a change in mineralogy from aragonite to calcite (Higgins et al., 2018, Pruss et al., 2018) because aragonite precipitation imparts a larger negative isotopic fractionation on Ca than does calcite. Although possible, a shift from predominantly aragonitic to calcitic mineralogies is unlikely because Mg/Ca ratios in Cretaceous fluid inclusions suggest that calcite was the dominant CaCO_3 polymorph precipitated by non-skeletal carbonates (Stanley, 2006).

3.6.4 Precipitation rate change

If the $\delta^{44/40}\text{Ca}$ variation is not a function of changes in mineralogy, it may instead be attributed to a change in the carbonate precipitation rate. That is if LIPs were erupting and

outgassing CO₂, seawater pH would decrease resulting in increased acidification, and decreasing the amount CO₃²⁻ precipitated (DuVivier et al. 2015). DuVivier et al. (2015) proposed this as the possible mechanism for the small positive $\delta^{44/40}\text{Ca}$ excursion observed in OAE 2. Also, increased CO₂ in turn increases the rate of continental weathering, likely resulting in greater Ca delivery into the ocean. This could have potentially affected the precipitation and fractionation of Ca isotopes.

The partition coefficient for Sr incorporation into CaCO₃ may increase as the precipitate rate increases (Tang et al., 2008; Bohm et al., 2012), and similarly, the Ca isotope fractionation factor may increase with the precipitate rate. This issue is currently under debate as summarized in Lau et al. (2017), Table 3 (e.g. Tang et al., 2008; DePaolo, 2011; Nielsen et al., 2012; Watkins et al., 2017; cf. Lemarchand et al., 2004; Gussone et al., 2005; AlKhatib and Eisenhauer, 2017a and 2017b). Additionally, laboratory studies have shown that stable Sr isotope compositions ($\delta^{88/86}\text{Sr}$) may also change with changing carbonate precipitation rate (Bohm et al., 2012).

Unlike the cross plot of $\delta^{44/40}\text{Ca}$ and [Sr] which so far shows no correlation (Fig. 3.7A), the $\delta^{44/40}\text{Ca}$ vs $\delta^{88/86}\text{Sr}$ is expected to show a strong correlation if the variation in the $\delta^{44/40}\text{Ca}$ are precipitation rate driven. The $\delta^{44/40}\text{Ca}$ vs $\delta^{88/86}\text{Sr}$ from the Iona-1 record thus far does not show the expected slope when Ca and Sr isotope fractionation factor vary with calcite precipitation (Fig. 3.7B). Instead, the result of this cross plot shows no correlation ($R^2 = 0.008$, $p\text{-value} = 0.56$).

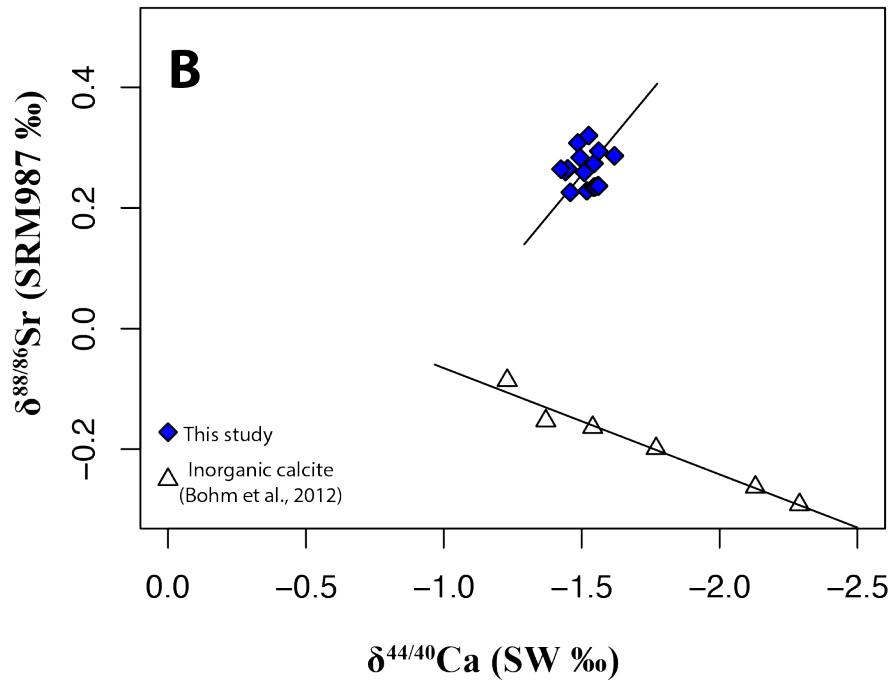
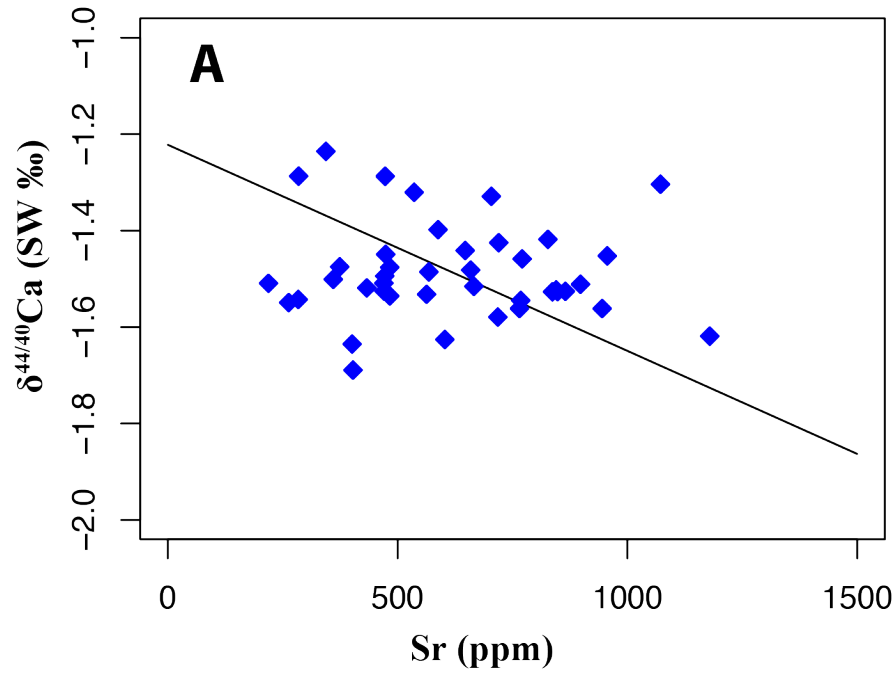


Figure 3.7: Cross plots of Sr concentration and $\delta^{44/40}\text{Ca}$ (A; R^2 : 0.008, p-value: 0.57) and $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ (B; R^2 : 0.001, p-value: 0.89).

3.6.5 Resolution of the data

The $\delta^{88/86}\text{Sr}$ data acquired so far is of lower resolution compared to the other isotope data and such it could have an effect on the interpretation presented here. Further $\delta^{88/86}\text{Sr}$ on the Iona core might results is needed for a robust interpretation and this might results in a reevaluation of the interpretation presented here.

3.6.6 Predictions and expected outcome

If the carbonate precipitation rate increased significantly at the onset of OAE 2, $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ would be predicted to show a positive correlation (Bohm et al., 2012). If they do not correlate, then other mechanisms must account for the positive $\delta^{44/40}\text{Ca}$ excursion during OAE 2, such change in temperature as fractionation factor also increases with temperature. Others have argued a decrease in Ca isotope fractionation but still having a positive $\delta^{44/40}\text{Ca}$ excursion can also be expected (Gussone et al., 2005; Tang et al., 2008; DePaolo, 2011; Sime et al., 2005). The precipitation rate change in natural samples has so far only been demonstrated in one study during OAE 1a (Wang et al., 2021) and will be examined upon acquisition of the complete data from the Iona-1 core. Because changes in ocean temperature affect how the respective isotopes of a given element fractionate during uptake (Tang et al., 2008).

3.7 Conclusion

A new high-resolution $\delta^{44/40}\text{Ca}$ isotope during OAE 2 was constructed from carbonate fractions of the Iona-1 core in the southern WIS. The $\delta^{44/40}\text{Ca}$ shows a positive excursion at the onset of OAE 2 similar to the previous study (Du Vivier et al., 2015) from the Portland core. However, the Iona-1 data is more complete and fills in a time gap that could not be captured by the Portland data due to a hiatus around the onset of OAE 2 in the Portland core. The $\delta^{44/40}\text{Ca}$ trend cannot be explained by changes in continental weathering, thus, to help explain and understand the response of the Ca isotopes, the $\delta^{88/86}\text{Sr}$ was measured. So far, the $\delta^{88/86}\text{Sr}$ record from the Iona-1 core does not mimic the $\delta^{44/40}\text{Ca}$. Cross plots of the $\delta^{44/40}\text{Ca}$ and $\delta^{88/86}\text{Sr}$ do not show a rate dependent-shift in fractionation expected, this in part could be due to the low resolution of the $\delta^{88/86}\text{Sr}$. Upon completion of the measurements within the OAE 2 section, better prediction can be made on the precipitation rate changes as well as comparison with studies in the end Permian (Wang et al., 2019) and OAE 1a (Wang et al., 2021).

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CONCLUSION

This dissertation addresses three aspects about understanding Ocean Anoxic Event 2 using multi-isotopes on the Iona-1 core in West Texas. First, was the role of weathering in nutrient delivery into ocean and if it can be quantified. Secondly, the growth of anoxia during this period and finally to understand the Ca isotope response during OAE 2 as well as its driving forces during this time.

In the first chapter, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater during OAE 2 was reconstructed from the carbonate fraction of the Iona-1 core in the southern WIS. The overall trend is one of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ before OAE 2 followed by a decreasing trend in the early part of OAE 2, a period of no change in $^{87}\text{Sr}/^{86}\text{Sr}$ in the middle part of OAE 2, and a resumption of the declining trend in $^{87}\text{Sr}/^{86}\text{Sr}$ for the remainder of OAE 2. The new $^{87}\text{Sr}/^{86}\text{Sr}$ data fill in missing details for the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve over this time interval, resolving questions about the timing and magnitude of change in hydrothermal and continental weathering fluxes of Sr to the oceans during OAE 2. The data also revealed for the first time that the decrease $^{87}\text{Sr}/^{86}\text{Sr}$ is synchronous with the decrease in the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater, the benchmark proxy for tracing massive volcanism during OAE 2. The declining trend in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ pauses in the middle of OAE 2 for about 150kyr, which is interpreted to reflect the end of at this time, which allows effects of increased continental weathering fluxes of Sr to the oceans to become visible in the record of changing seawater $^{87}\text{Sr}/^{86}\text{Sr}$ for the first time since onset of OAE 2. An ocean Sr box model was employed to simulate the change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ through OAE 2, and to quantify hydrothermal and continental weathering flux changes. The 1.8–1.85-times increase in the continental weathering flux during OEA 2 estimated using Sr isotopes in this study is smaller than threefold increase using Ca and Li isotopes as continental weathering

proxies. This lower continental weathering rate has important ramifications for how OAE 2 and OAEs in general originate and evolve, and what controls nutrient delivery to the oceans during these events.

In the second chapter, Cr isotopes was used to understand the redox changes of the ocean during OAE 2. The carbonate derived $\delta^{53}\text{Cr}$ values produced a negative excursion, similar to those obtained in two previous studies. However, the carbonate $\delta^{53}\text{Cr}$ values obtained from the Iona-1 core has a smooth and more complete record than was previously obtained, thus allowing for investigation of the effect of onset of LIP on the Cr record. Importantly, the study revealed two things, first, the negative $\delta^{53}\text{Cr}$ excursion lags behind the decrease in $^{187}\text{Os}/^{188}\text{Os}$ values by 70 kyr, a detail not captured in the other studies due to resolution and hiatus around the onset of OAE 2 and finally, that the Cr isotope proxy during OAE 2 is recording changes in hydrothermal inputs and not anoxia.

In the final chapter, a new high-resolution $\delta^{44/40}\text{Ca}$ isotope during OAE 2 shows a positive excursion at the onset of OAE 2 similar to the previous study from the Portland core. As with the other proxies, the Iona-1 data is more complete and fills in a time gap that could not be captured by the Portland data due to a hiatus around the onset of OAE 2. The $\delta^{88/86}\text{Sr}$ was measured so as to help understand the Ca isotope trend. However, due to the resolution of the $\delta^{88/86}\text{Sr}$ record obtained so far, the results remain inconclusive.

Overall, this study showed that, careful extraction of the carbonate fractions from the Iona-1 core and high resolution of the data, was able to obtain signal that was not captured in previous studies. Also, the increase weathering at the onset of OAE 2 was smaller than previously thought. Additionally, the Cr proxy during OAE 2 does not track the growth of anoxia but hydrothermal inputs into the ocean.