The timing and influence of massive volcanism to Ocean Anoxic Event 2 in the Western Interior Sea

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Introduction

Despite considerable study of the Cenomanian-Turonian Boundary (CTB; 93.9 ± 0.15 Ma) in the Western Interior Basin (WIB) of North America and around the world, the timing and influence of massive volcanic events and their relationship to ocean anoxia remains inadequately resolved. This study will combine multiple new compositional and geochemical datasets through the Upper Cretaceous Greenhorn Formation during Ocean Anoxic Event 2 (OAE 2) to assess chronology and impact of volcanism in the Western Interior Sea (WIS).

Geologic Background

Earth's oceans have experienced periods of substantial oxygen depletion throughout the Phanerozoic (Jenkyns, 1980). First recognized in the central and western Pacific Ocean during the 1973 Deep Sea Drilling Project (DSDP), CTB aged black and green carbonate sediments revealed significant organic enrichment and other indicators of oxygen-depleted burial conditions (McCave, 1979). Later, this interval was extrapolated to the Atlantic and Caribbean Basins leading Schlanger and Jenkyns (1976) to coin the term "Oceanic Anoxic Events" or OAE's to reflect their global significance. The past fifty years have produced a body of work compiled from locations around the world revealing significant marine anoxic events interpreted to be global oxygen and carbon cycle perturbations (Percival et al., 2015). While the characteristics of each OAE are variable, and even vary between time-correlative sites, pronounced excursions in stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios typify each event (Scholle and Arthur, 1980; Singh et al., 2022). Simultaneous, widespread organic-rich sediment deposition is also characteristic of OAE's (Arthur and Sageman, 1994) suggesting low oxygen availability. However, lithology and total organic content (TOC) are highly variable.

OAE 2 begins in the latest Cenomanian as a severe, environmental perturbation expressed globally as an extreme, positive carbon isotopic excursion (CIE) of $\delta^{13}C > 3 - 7‰$ VPDB (Figure 1; Arthur et al., 1987). Widespread organic matter burial, marine anoxia/euxinia, pronounced increases in sea surface temperature (SST), elimination of most benthic foraminifera, and increases in proxy pCO_2 concentration all occur within a few thousand years (Jenkyns, 2010). These conditions persist into the early Turonian but are not uniform throughout the ~600 – 800 ka duration. A transitory cooling phase known as the Plenus Cold Event (or PCE; O'Connor et al., 2020) echoes cool conditions and more negative $\delta^{13}C$ values immediately prior to OAE 2 (Du Vivier et al., 2014; Jenkyns et al., 2017). Both cooling pulses within the overall Cretaceous Thermal Maximum warming trend are coincident with a pronounced rise in proxies associated with volcanism (O'Connor et al., 2020). No less than five active massive volcanic systems, known as Large Igneous Provinces (LIPs), were active immediately prior to and throughout the duration of OAE 2 (Ernst and Youbi, 2017). The sudden enrichment of proxies associated with elevated pCO_2 in the atmosphere and the introduction of metals predominantly associated with mafic (Fe and Mg) intrusive bodies also creates a compelling argument for LIP volcanism triggering OAE 2. Due to this correspondence, massive volcanic eruptions are widely considered to have been responsible for OAE 2 (Percival et al., 2020 and references therein). While the expression of OAE 2 is variable and nuanced, the global and time-correlative nature of the extreme CIE signal strongly advocates for a worldwide triggering mechanism (Jenkyns et al., 2017).

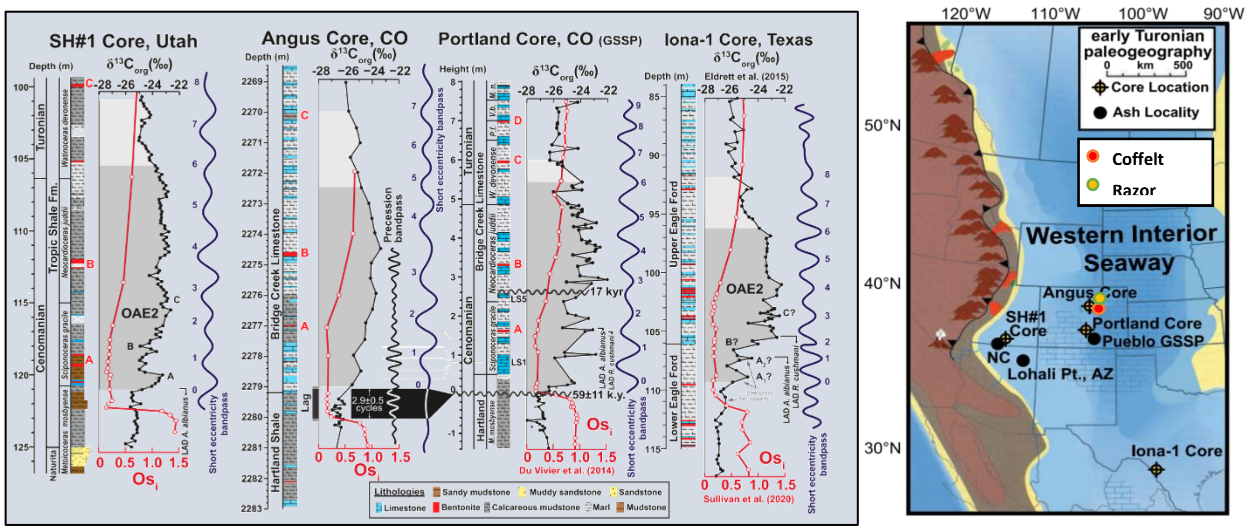

Figure 1. Early Turonian paleogeography of the Western Interior Sea, USA (right) showing localities of cores and stratigraphic columns (left) of cores discussed for this study. Note location of Coffelt 5-61-35 (red) and Razor 25-2514H (yellow) locations within the DJ Basin. Core descriptions and orbital bandpass filters plotted alongside $\delta^{13}C$ and initial Os isotope chemostratigraphy data reveal hydrothermal/LIP signature prior to CIE of OAE 2. Modified from Jones et al. (2021; and references therein).

Detailed isotopic and elemental proxy studies of OAE 2 in the northern Tethys highlight the two opposing trend negative perturbations immediately preceding the initial positive $\delta^{13}C$ "build-up" phase and immediately prior to the "plateau" phase (the PCE). During these reversals, ^{192}Os, $\delta^{53}Cr$, and Hg values change suggesting a more mafic provenance signal while elemental redox proxies (i.e. Mo and U) indicate a more ventilated water column and oxygenated bottom conditions. Proxy sea surface temperature data (TEX_{86}) suggest a ~4 °C cooling directly correlated to initial ^{192}Os isotope enrichment (Jones et al., 2021; Percival et al., 2020). An enrichment of redox sensitive trace elements and a continuation of positive $\delta^{13}C$ values suggest a return to warming and anoxia immediately above the PCE. $\delta^{53}Cr$ and Hg return to pre-OAE 2 values earlier than the stabilization of $\delta^{13}C$ values marking the end of OAE 2 suggesting LIP activity diminished while organic matter burial, marine anoxia, and elevated pCO_2 persist through self-supporting feedback mechanisms. An initial pulse(s) of volcanism may have reached a tipping point in the atmosphere, temporarily dimming solar radiation by increasing particulate matter in the atmosphere before increased pCO_2 created a superseding greenhouse effect. Massive volcanic activity may produce immediate transient cooling (such as the PCE), but the addition of significant carbon volumes to the ocean-atmosphere system may eventually produce an overwhelming positive feedback mechanism driving global hothouse conditions.

Significance

Establishing first-order relationships during global carbon cycle perturbations are critical, not only to better understand how ancient marine environments adapted but also to better predict how modern ecosystems will behave. Cretaceous oceans and epicontinental seas responded to the increase in atmospheric pCO_2 by absorbing and depositing massive volumes of carbon into what are now significant source rocks for petroleum systems around the world. The Tropic Shale, Mancos Shale, and Hartland Shale Member of the Greenhorn Formation in the WIB all see pronounced yet variable degrees of organic matter enrichment (Arthur et al., 1987). However, the CTB was a dynamic time. Contemporaneous thirdorder eustatic changes, de-stratification of the water column, and increased Cordilleran tectonism all result in locally complex depositional controls that can obscure the nature and sequence of OAE 2 (Eldrett et al., 2017). Previous studies have also suffered from incomplete preservation, especially in well-studied base Turonian Global Boundary Stratotype Section and Point (GSSP) and the USGS Portland 1 core near Pueblo, CO (Jones et al., 2021) that further conceal the precise timing and nature of OAE 2 (Figure 1). Acquiring a new, detailed chronology of events using more complete stratigraphic sections, such as those in the Denver-Julesburg (DJ) Basin, will help to resolve decades-old questions on the timing and mechanisms of anoxia during OAE 2.

Using detailed geochronology and sensitive, high-fidelity proxies for marine anoxia and volcanic input, this study will help untangle the timing and relative influence of volcanism during OAE 2 and particularly the PCE having received comparatively little study in the WIS. Two wells, the Cofflet 5-61-35 and Razor 25-2514H with cores cutting the Greenhorn Formation in the Denver-Julesburg (DJ) Basin (Figure 1) will be used to test the following hypotheses:

1) Signals of proxy volcanic input will increase immediately prior to the initial CIE of OAE 2 and prior to the Plenus Cold Event.
2) Volcanic signals will be short lived and diminish prior to the return of CIE to pre-OAE 2 levels.
3) The relative strength of the volcanic proxy signals will correlate with not only to the severity of the CIE but also to the enrichment of elemental proxies of anoxia.

Plan

This study will include high-resolution core descriptions and laboratory analyses including thin section petrography, x-ray diffraction (XRD) mineralogy, x-ray fluorescence (XRF) and high-resolution inductively coupled mass spectroscopy (HR-ICPMS) elemental composition, whole rock dry pyrolysis, and $\delta^{13}C$ isotope analyses. $^{40}Ar/^{39}Ar$ geochronology of bentonites in conjunction with $^{187}Os/^{188}Os$-chemostratigraphy will assess timing and depositional rates while elemental proxies (e.g. V, Ni, Mo, U, Cr, ^{192}Os, $\delta^{53}Cr$, Hg) will assess the degree of anoxia and nature of volcanic influence in the water-column. Results from the two study cores will then be correlated to the published proximal-distal transects in the WIB including the Angus, Portland 1 (Pueblo GSSP), SH#1 (Tropic Shale), and Iona-1 (Eagle Ford Formation) cores to assess timing depositional hiatuses (Figure 1). Core descriptions, XRD, XRF, pyrolysis, and $\delta^{13}C$ isotope analyses (Razor 25-2514H) are now complete as of writing. Each identified lithofacies has been sampled for thin sectioning and select samples are currently undergoing scanning electron microscopy (SEM) automated mineralogy via third-party laboratory. Estimated return of thin sections is now mid-May, 2022. Additional sampling for data resolution may be necessary and may include solvent extracted pyrolysis, LECO TOC (for Hg normalization), and continuous XRF of the Razor 25-2514H core. These analyses will be completed using in-house Colorado School of Mines facilities. Sampling for specialty elemental and isotopic datasets ($^{40}Ar/^{39}Ar$, $^{187}Os/^{188}Os$, ^{192}Os, $\delta^{53}Cr$, and Hg) is complete and material is currently prepped for transport to respective laboratories once funding is secured. These specialty analyses are available via third-party laboratories and are estimated to be available mid-July if received in early May, 2022.

All funds generously awarded by the Rocky Mountain Section - Society for Sedimentary Geology would be used for Os isotopic analysis of sediment from specialty third-party labs. Shipping to destination laboratories will be covered using supporting funds from the Colorado School of Mines MUDTOC Consortium. Please see Figure 2 for a project budget and current received funds.

Matson PhD Thesis Project: The Timing and Influence of massive volcanism during Ocean Anoxic Event 2 (OAE 2) in the Western Interior Sea

Coffelt	Razor	Item	Vendor	Quantity	Unit Cost ($USD)	Total ($USD)	Details/Justification	Funding Requst (Agency)	Funded Amount/request	Amount Received*
Laboratory Services										
☑	☐	Thin Sections	Wagner Petrographic	25	$ 30.00	$ 750.00	Coffelt core: Standards, blue UV epoxy, calcite stain. Precut and student discount. *CSM TS Lab offline.	**SEPM Foundation (received)**	**$ 750.00**	**$ 750.00**
☑	☐	Automated (SEM) mineralogy	Vidence Inc	10	$ 275.00	$ 2,750.00	Coffelt core: includes prep with CL overlay; sample prep by researcher	**MUDTOC Consortium (approved)**	**$ 2,750.00**	**$ 2,750.00**
☑	☑	Pyrolysis & Calculated TOC	In-house CSM	65	$ -	$ -	Coffelt and Razor cores; infilling existing data for resolution. No cost. Prep and analysis by researcher with MUDTOC consortia instrument.	**MUDTOC Consortium (approved)**	**$ -**	**$ -**
☐	☑	Continuous XRF	In-house CSM/USGS	480	$ -	$ -	Razor core: No cost. Provided through CSM/USGS with collaboration on reference calibations.	**CORE Consortium (appoved) no cost**	**$ -**	**$ -**
☑	☑	HR-ICPMS (CEMS)	SGS/ALS Bids	35	$ 55.00	$ 1,925.00	Coffelt and Razor cores. Sampling and initial prep by researcher. Minimum Thermo Neptune PLUS w/ ESI APEX system.	*AIPG (applied)*	*$ 2,000.00*	$ -
☑	☑	Hg/TOC	SLAC (Stanford), Oxford, other vendor	25	$ 23.50	$ 587.50	Coffelt and Razor cores. Coinside with TS points sample points. Lumex Portable Mercury Analyzer coupled with Pyrolyzer. Sample pricing based on current lowest bid.	*MUDTOC Consortium (unapproved)*	*$ 587.50*	$ -
☐	☑	XRD Mineralogy bulk and total clay	CSM	10	$ 50.00	$ 500.00	Razor cores: infilling existing data for resolution. Sampling by researcher. Unit cost estimated from time.	**MUDTOC Consortium (approved)**	**$ 500.00**	**$ 500.00**
☑	☑	40Ar/39Ar Geochronology	CSM/USGS	25	$ 24.25	$ 606.25	USGS Argon geochronology lab at Denver Fed Center. Unit cost estimated and based on analysis time. 23 bentonites in plus x-bentonite. Sampling by researcher.	*Colorado Scientific Society (applied)*	*$ 600.00*	$ -
☑	☑	C-isotopic prep and analysis	CSM	210	$ 5.00	$ 1,050.00	Coffelt and Razor cores; infilling existing data for resolution. Sampling by researcher. Unit cost estimated from time.	**MUDTOC Consortium (approved)**	**$ 1,050.00**	**$ 1,050.00**
☑	☑	Cr-isotopic prep and analysis	SGS/ALS	55	$ 80.00	$ 4,400.00	Coffelt and Razor cores: Sample pricing based on current lowest bid by ALS. Sampling by researcher.	*AAPG Grant-In-Aid (appied)*	*$ 4,400.00*	$ -
☑	☑	(Re)Os/Os-isotopic analysis	SGS/ALS/AIRIE (CSU)	10	$ 195.00	$ 1,950.00	Coffelt and Razor cores: sample pricing based on current lowest bid by ALS. Sampling by researcher.	*RMS-SEPM Donald L. Smith Grant*	*$ 2,000.00*	$ -
								TOTAL REQUESTS (REQUEST/RECEIVED)	**$ 14,637.50**	**$ 5,050.00**
					TOTAL EST BUDGET	**$ 14,518.75**		**DIFFERENCE**	$ 118.75	$ 9,587.50
								Italics indicate requested amounts not yet receved and **bold** indicates received/approved amounts		*As of March 30, 2022

Figure 2. Budget for laboratory analyses of Matson Thesis Project: The timing and influence of massive volcanism during Ocean Anoxic Event 2 (OAE 2) in the Western Interior Sea. Italicized Funding Request entries denote funds applied for but not yet awarded. Bold Funding Request entries denote received funds. Marked in orange are the Os isotope analyses that would be covered from a potential generous award from the RMS-SEPM Donald L. Smith Research Grant. Values accurate as of March 30, 2022.

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