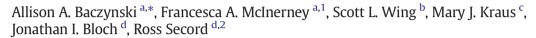
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Constraining paleohydrologic change during the Paleocene-Eocene Thermal Maximum in the continental interior of North America



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ABSTRACT

Ouantifying the relationship between carbon cycle perturbations and the hydrologic cycle in the geologic past is crucial to accurately modeling how future anthropogenic carbon emissions and resulting radiative forcing might affect the hydrologic cycle. Interpreting changes in proxy records for insight into paleohydrologic change is complex, and documented records of paleohydrologic response to past global warming are rare. We use the relationship between two independent proxy records, the stable isotope ratios of hydrogen in *n*-alkanes and oxygen in tooth enamel of Coryphodon, to examine paleohydrologic change in the continental interior of North America during the Paleocene-Eocene Thermal Maximum (PETM) hyperthermal ~56 Ma. The Coryphodon δ^{18} O record allows us to infer shifts in surface water isotope values through time by applying an empirical relationship between tooth enamel and precipitation δ^{18} O values. Precipitation δ^{18} O values increase by ~4‰ during the PETM, but *n*-tooth values increase by ~4‰ during the PETM. alkane hydrogen isotope ratios show no directional change during the PETM. We explore multiple hypotheses that could explain the differences between the isotope records, including a change in apparent fractionation as a result of plant community change, a shift in the slope of the local meteoric water line, a change in the season of rainfall, or a shift in the season of lipid production. We model the changes that would be required to reconcile the isotope records for each hypothesis and evaluate the likelihood of each of the scenarios. We posit that the most likely hypothesis for the observed differences between the isotope records is a change in either the season of rainfall or the season of lipid production during the PETM.

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1. Introduction

One of the important uncertainties in climate change projections is how the hydrologic cycle might respond to increasing pCO_2 and temperature. Although climate models are improving in their characterization of precipitation patterns at a global scale, there remains a significant amount of uncertainty at the regional scale (Collins et al., 2013), particularly for the interior of continents (Solomon et al., 2009). Theoretical calculations and global climate models predict that positive radiative forcing from rising pCO_2 levels will increase the prevalence of extreme precipitation events and that both floods and droughts will vary both spatially and temporally (Collins et al., 2013).

The concentration of carbon dioxide in the atmosphere affects global climate not only due to radiative forcing, but also by its influence on plant physiology. Plants regulate the opening and closing of stomata, pores on the surface of the leaf, based on environmental conditions including temperature, humidity, and availability of carbon dioxide. When carbon dioxide concentrations are high, stomata open less and transpiration decreases. The reduction in moisture flux from Earth's surface to the atmosphere results in higher temperatures near the surface (Betts et al., 2007; Ciais et al., 2013). While it is unknown exactly how much physiological forcing will contribute to overall climate change, recent studies have suggested that the indirect physiological forcing of plants will have a greater influence on global temperature than the direct radiative effects of carbon dioxide (Cao et al., 2010). Characterizing hydrologic change in the geologic past will expand our understanding of how Earth's climate and ecosystems respond to perturbations of the



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carbon cycle and associated global warming and is key to understanding how future anthropogenic carbon emissions may influence the hydrologic cycle.

One of the largest and most rapid natural perturbations to the global carbon cycle occurred ~56 Ma at the Paleocene-Eocene boundary. This event, known as the Paleocene-Eocene Thermal Maximum (PETM), was an abrupt (\leq 20,000 years), transient (<200,000 years) episode of extreme (~5 to 8 °C) global warming that is recognized as the warmest period of the Cenozoic Era (Kennett and Stott, 1991; McInerney and Wing, 2011; Sluijs et al., 2007; Zachos et al., 1993; Zachos et al., 2001). The late Paleocene through early Eocene has long been recognized as a period of biotic change, which has been primarily attributed to rapid temperature change and increased pCO_2 . However, associated changes in the hydrologic cycle, such as the amount and/or seasonality of precipitation, may have been a key driver of the observed terrestrial ecosystem changes.

The degree to which precipitation patterns were altered during the PETM is poorly understood, with interpretations of hydrologic proxies from sites across the globe ranging from considerably wetter conditions to significantly drier conditions and everything in between. An increase in the abundance of kaolinite and terrestrial palynomorphs along the northeastern margin of the United States, and in New Zealand and Antarctica, have been cited as evidence for enhanced erosion and runoff, which in turn have been attributed to increased precipitation and wetter PETM conditions (Cramer et al., 1999; Crouch et al., 2003; Gibson et al., 2000; Kaiho et al., 1996; Robert and Kennett, 1994). Some general circulation models and models of carbon cycling processes have suggested higher relative humidity in continental interiors during the PETM (Bowen et al., 2004; Huber and Sloan, 1999). Yet other studies have suggested regional variations, with greater relative humidity at higher latitudes and more arid conditions at subtropical latitudes (Bowen and Bowen, 2008; Pagani et al., 2006; Wing et al., 2005). Previous paleobotanical, paleopedologic, and isotopic studies from the PETM in the southeastern Bighorn Basin, WY, have indicated that the continental interior of North America may have experienced alternating episodes of wet and dry conditions during the PETM (Kraus et al., 2013; Kraus and Riggins, 2007; Secord et al., 2012; Smith et al., 2007; Wing et al., 2005). Additionally, Schmitz and Pujalte (2003, 2007) have proposed generally arid PETM conditions, but with an increase in seasonally extreme precipitation in mid-latitude continental Spain. Changes in fluvial deposition in western Colorado also suggest that flooding was common during the PETM and may indicate greater variability in the intensity of rainfall events (Foreman et al., 2012). More data are required to evaluate whether such differing interpretations reflect real spatial variations in precipitation, different sensitivities or seasonal biases of the individual proxies, or possibly misinterpretation of some paleohydrologic proxy data

n-Alkanes are frequently used as a paleoclimate proxy because of their high preservation potential and resistance to isotopic exchange (Pedentchouk et al., 2006; Schimmelmann et al., 2006; Sessions et al., 2004). High molecular weight *n*-alkanes with a marked predominance of odd-over-even carbon chain lengths (C25 to C35) are important constituents of the epicuticular waxes of vascular plants (Eglinton and Hamilton, 1967) and can serve as indicators of terrestrial plant input. The hydrogen incorporated into *n*-alkanes originates from meteoric water, which is influenced by temperature, humidity, evaporation, rainfall amount and water vapor source (Craig, 1961; Craig and Gordon, 1965; Gat, 1996; Rozanski et al., 1993). Because modern *n*-alkane hydrogen isotope (δD) ratios are highly correlated with the hydrogen isotopic signature of meteoric water at the time of their biosynthesis (Kahmen et al., 2011; Sachse et al., 2010; Sachse et al., 2009; Tipple et al., 2013), shifts in δD ratios of *n*-alkanes from geologic records are often equated to shifts in paleoclimate.

The *n*-alkane δD records from the Bighorn Basin, Lomonosov Ridge in the Arctic Ocean, and Tanzania suggest a positive shift in δD values at the onset of the PETM, which has been offered as evidence for drier conditions in mid-latitudes and increased moisture transport to the Arctic (Handley et al., 2008; Pagani et al., 2006; Smith et al., 2007). Conversely, records from Italy, France, New Zealand and Columbia/ Venezuela suggest a negative shift in δ D values at the onset of the PETM (Garel et al., 2013; Handley et al., 2011; Jaramillo et al., 2010; Krishnan et al., 2015; Tipple et al., 2011). The negative shift in δ D values has been interpreted as indicating a wetter or more humid climate state at some sites (Garel et al., 2013; Handley et al., 2011). Additionally, the shift to more positive δ D values prior to the onset of the CIE in some records suggests there may have been significant changes in the hydrologic cycle prior to the PETM (Garel et al., 2013; Tipple et al., 2011).

Interpreting changes in paleohydrology using *n*-alkane δD records is challenging because the isotope ratios of modern plant lipids reflect not only the δD ratio of meteoric water but also the D-enrichment of leaf water resulting from evaporation and/or transpiration and isotopic fractionation that occurs during *n*-alkane biosynthesis (Kahmen et al., 2013a; Kahmen et al., 2013b; Sachse et al., 2012; Sachse et al., 2006; Smith and Freeman, 2006). This makes it extremely difficult, if not impossible, to interpret climate regime based solely on shifts in lipid δD values. Furthermore, the high molecular concentrations required for *n*-alkane δD analysis restrict the number of measurements that can be made, and the few PETM *n*-alkane δD records that do exist commonly have a much lower resolution than the corresponding *n*-alkane carbon isotope ($\delta^{13}C$) curves.

Previous studies have not been able to independently examine changes in plant community composition and the isotope ratios of precipitation, both of which contribute to the *n*-alkane δD signature. In this study, we measure the hydrogen isotope values of *n*-alkanes and explicitly characterize these effects. Specifically, we consider how the shift from a mixed angiosperm/conifer to predominantly angiosperm flora and the increase in proportion of monocots (Smith et al., 2007; Wing and Currano, 2013; Wing et al., 2005) would affect apparent fractionation between source water and leaf wax lipids. We also independently constrain changes in the isotopic composition of precipitation by applying an empirically derived relationship between tooth enamel and precipitation oxygen isotope (δ^{18} O) values to *Coryphodon* tooth enamel δ^{18} O values (Kohn and Dettman, 2007). The δ^{18} O and δ D isotope profiles differ, suggesting that the *n*-alkane record does not directly record changes in annual precipitation isotope ratios. We explore several explanations for reconciling the isotope records by modeling changes in the local meteoric water line, seasonality of precipitation, and apparent fractionation, and assess the likelihood of each scenario. The ability to independently constrain precipitation isotope values and changes in plant community allows a unique exploration of paleohydrologic change during the PETM.

2. Methods

2.1. Study area and sample collection

The Bighorn Basin, WY (Fig. 1) preserves an unusually complete and expanded continental stratigraphic record of the early Paleogene (Bown, 1980; Wing, 1998). Extensive sedimentological, geochemical, and paleontological research has established a strong lithostratigraphic, biostratigraphic, and chemostratigraphic framework for the PETM in the southeastern Bighorn Basin (see Baczynski et al., 2013). Bulk organic carbon, *n*-alkane, and mammalian tooth enamel carbon isotope records from the southeastern Bighorn Basin, WY independently document the negative carbon isotope excursion (CIE) associated with the PETM. A shift to more negative carbon isotope values marking the onset of the PETM is corroborated by biostratigraphic data, with the first appearances of earliest Eocene (Wa-0) mammals. Likewise, the carbon isotope recovery in *n*-alkanes and tooth enamel is coincident with a change in floral composition and a faunal shift from biozone Wa-0 to Wa-1 (Baczynski et al., 2013; Baczynski et al., 2016; Secord et al., 2012). The

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