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LARGE IGNEOUS PROVINCES AND EARTH'S CARBON CYCLE: LESSONS
FROM THE LATE TRIASSIC AND RAPIDLY EMPLACED CENTRAL ATLANTIC
MAGMATIC PROVINCE

by

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ABSTRACT OF THE DISSERTATION

Large Igneous Provinces and Earth's Carbon Cycle: Lessons from the Late Triassic and
Rapidly Emplaced Central Atlantic Magmatic Province

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Using stable carbon isotopes of soil carbonates, I demonstrate that the eruption of the Central Atlantic Magmatic Province (CAMP) resulted in a transient perturbation of atmospheric $p\text{CO}_2$ in the Late Triassic. I show evidence of a discrete $p\text{CO}_2$ pulse (roughly a doubling) immediately after the first CAMP flow-unit preserved in the Newark rift basin, followed by a ~ 200 kyr falloff toward pre-eruptive concentrations, a pattern repeated above the second and third flow-units. Observations from the Hartford basin indicate that $p\text{CO}_2$ had fallen to concentrations well below background by 400 kyr after the final eruptions in the earliest Jurassic. I use a simple geochemical model to demonstrate that this decrease below pre-eruptive background is most easily accomplished by the extrusion of $\sim 1.12 \times 10^7 \text{ km}^2$ of basalt into the equatorial humid belt, which effectively amplified the increase in global continental weathering rate by perhaps as much as 50%. These results indicate that LIPs can be overall net sinks for CO_2 . A test of the Late Triassic equilibrium state from a 33-My record of $p\text{CO}_2$ broadly shows a ~ 3 -fold decrease from the Carnian through the Rhaetian. This $p\text{CO}_2$ decrease is most consistent with the hypothesis that a Late-Triassic increase in continental area within the tropical humid belt, as a result of the slow northward migration of the Pangean

Supercontinent, lead to increased rates of continental weathering and CO₂ consumption.

A significant implication of this finding is that changes in degassing rate from variable ocean crust production are not driving the long-term decrease in pCO₂ because crustal production rates show little variability through the Late Triassic. Together, the results of this work lay the foundation for a revision of our understanding regarding the driving mechanisms behind Earth's long-term carbon cycle toward a greater emphasis on weathering processes.

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Chapter 1

Introduction to the Dissertation

1.1. Atmospheric pCO₂ over geologic time

The balance between incoming solar energy and outgoing long-wave radiation dictates Earth's surface temperature. Because this balance is controlled primarily by atmospheric greenhouse gases, determining past concentrations of these gasses, particularly during times of global climatic extremes, is a central focus of paleoclimate research. Carbon dioxide is the most studied greenhouse gas because of its effectiveness in absorbing long-wave radiation, its inter-connection with many geologic and biologic processes, and its relatively long residence time (Berner et al., 1983). Because of the effectiveness of CO₂ at regulating Earth's climate over geologic scales (e.g., Royer et al., 2004), it is important that we understand the dynamic sources and sinks of CO₂ over a variety of timescales.

On the million-year scale, equitable climates at Earth's surface are controlled by the balance between CO₂ outgassed at mid-ocean ridges and volcanoes, and the consumption of that CO₂ by weathering reactions on the continents. Because CO₂ exerts a fundamental control over temperature, and temperatures influence precipitation patterns (e.g., Manabe and Wetherald, 1980), and the rates of continental weathering (see Kump et al., 2000, for review), an increase in atmospheric pCO₂ ultimately leads to an increase in chemical weathering. Increased weathering more rapidly consumes CO₂, leading to an eventual decrease in atmospheric pCO₂, which constitutes a 'thermostat' that keeps Earth's temperature within a stable range over long timescales (Walker et al., 1981).

In this dissertation I lay the groundwork for a significant revision of our understanding of the long-term carbon cycle; how it can be perturbed on very short temporal scales; and how the distribution of continental area, and variability of lithologies on Earth's surface, can determine CO₂ sink-side processes. I first detail the method used in this work for estimating pCO₂ from soil carbonates, where my own contribution to the proxy makes systematic pCO₂ estimates more internally consistent (Chapter 2). I then take advantage of a natural experiment that reveals some fundamental behaviors of the carbon cycle (Chapters 3 and 4). Finally, I determine the long-term (10⁷-year) driving mechanisms behind the evolution of pCO₂ through the Late Triassic, which has implications for our understanding of the long-term regulation of equitable climates on Earth's surface during other time periods (Chapter 5).

1.2. Problems to be addressed

A useful way of investigating a dynamic, feedback-controlled system such as Earth's carbon cycle is to perturb it with some transient forcing. In the third chapter of this dissertation I take advantage of a natural experimental perturbation of the carbon cycle that I show can be tracked using a proxy for atmospheric pCO₂: the eruption of a large igneous province (LIP). These volcanic episodes have the potential to severely perturb the Earth's climate system through the emission of gasses, most notably SO₂ and CO₂, which together may result in an immediate (1 – 10 year) cooling (Chenet et al., 2005; Robock, 2000; Self et al., 2005), followed by a longer-term (10² – 10⁵ year) warming (Wignall, 2001). Intriguingly, LIP volcanism is often temporally associated with mass extinction events throughout the Phanerozoic (i.e. Courtillot and Renne, 2003; White and Saunders, 2005; Wignall, 2001).

In Chapter 3 of this work, I closely examine the potential $p\text{CO}_2$ effect of the Late Triassic-earliest Jurassic Central Atlantic Magmatic Province, evidence of which is particularly well preserved as lava flows, sills and dikes in the rift basins of eastern North America. I test the hypothesis that LIP volcanism measurably alters the global carbon cycle through transient releases of CO_2 , followed by consumption of CO_2 via longer-term silicate weathering. I show evidence of a discrete $p\text{CO}_2$ effect due to each of the CAMP pulses recorded in the Newark Basin, followed by a ~ 200 kyr falloff toward pre-eruptive concentrations (Schaller et al., 2011a).

This work contains the first evidence that demonstrates an atmospheric $p\text{CO}_2$ effect directly attributable to LIP volcanism, and has generated interesting speculation on the sources and duration of the apparent CO_2 release (e.g., Rampino and Caldeira, 2011), which I argue must be on the order of 1000 years or less for the first eruptive pulse (see Chapter 3S or Schaller et al. (2011b)). Such a rapid release of CO_2 certainly must have environmental and temperature effects, but a causal relationship with the CO_2 pulse and the associated end-Triassic Extinction has not yet been demonstrated (see discussion in Chapter 6). Of greater interest from the carbon cycle perspective are the 10^5 -year decreases in $p\text{CO}_2$ immediately following each eruption, which I demonstrate are a fundamental response of the carbon cycle.

The million-year impact of rapidly emplacing highly weatherable basaltic material in the equatorial humid belt is the focus of Chapter 4. Dessert et al. (2001) use a carbon cycle model to demonstrate that the eruption of the Deccan Traps resulted in a transient perturbation of the carbon cycle. They also show that if erupted in the correct location, the highly weatherable basalts would lead to a drawdown in $p\text{CO}_2$ to below pre-

eruptive background concentrations, due to the additional consumption of CO₂ by weathering the basalts themselves. A test of this million-year scale effect following emplacement of the CAMP in the strata of the Hartford basin in eastern North America, shows that pCO₂ is reduced well below pre-eruptive background (Schaller et al., 2011c).

Geochemical modeling (using modified COPSE code) demonstrates that the rapidity of the post-eruptive pCO₂ decreases in the Portland Formation of the Hartford basin, and the fall to concentrations below background, can be accounted for by a 1.5-fold amplification of the continental silicate weathering response due to the presence of the CAMP basalts themselves. These results demonstrate that continental flood basalt may actually have an overall net-cooling effect on global climates due to a long-term net-decrease in pCO₂ to below pre-eruptive levels. Considering the transience of the observed LIP-induced degassing, this long-term sink of CO₂ may be the only long-lasting effect of a LIP eruption on Earth's carbon cycle.

In the final research chapter of this work (Chapter 5), I take a step back and look at the long-term 10⁷-year evolution of CO₂ in the Late Triassic. I empirically test the plausibility of two models for long-term changes in CO₂: Those models based on the BLAG-hypothesis (Berner et al., 1983) (e.g., GEOCARB (Berner, 1991)), which force atmospheric pCO₂ by changes in degassing from dynamic ocean crust production at mid-ocean ridges, compared to the Godderis et al. (2008) hypothesis that relates long-term changes in atmospheric CO₂ to changes in the distribution (and lithology) of continental area.

I present a 33-million year pCO₂ record through the Late Triassic into the earliest Jurassic that shows a ~3-fold decrease in pCO₂ over the interval, a period of time over

which the GEOCARB models show very little change. I find that this long-term decrease is most consistent with the Godderis et al. (2008) hypothesis, where the Late Triassic decrease in $p\text{CO}_2$ is linked to an drastic increase in the amount of continental area situated in the tropical humid belt, a result of the slow northward migration of the Pangean supercontinent. Overall, these results indicate that the long-term evolution of $p\text{CO}_2$ may be forced not by variable degassing from changing crustal production, but by variability in the rates of continental weathering due to the changing distribution of continental area with respect to the zones of active weathering at Earth's surface.

Each of these studies is a discrete test of a characteristic of the carbon cycle on a different timescale. Chapter 3 focuses on the instantaneous short-term effects of a degassing perturbation, while Chapter 4 tests the intermediate implications of placing a CO_2 'sponge' in the tropical humid zone where it may most effectively absorb atmospheric CO_2 . Chapter 5 gives us a sense of the driving forces behind geologic-scale changes in $p\text{CO}_2$, which may be primarily a function of sink-side processes. Together they make a compelling case that differential continental weathering may control Earth's climate over a wide range of timescales.

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Chapter 2

Using Stable Isotopes to Estimate $p\text{CO}_2$ from Pedogenic Carbonates

2.1. Introduction to the method

Throughout this work I use a method of $p\text{CO}_2$ reconstruction pioneered by Thure Cerling (Cerling, 1984; Cerling, 1992; Quade et al., 1989), which exploits a terrestrial environment that may be unique in its ability to record the conditions at Earth's surface outside of a body of water: Soil, or as used here in the geologic record, paleosols. The method takes advantage of the mixing between the atmospheric carbon reservoir above a soil and the biologically respired reservoir within a soil, and has been continually refined since its inception (Breecker et al., 2009a, 2010; Breecker et al., 2009b; Cerling, 1991; Cerling, 1992, 1999; Cerling and Hay, 1986; Cerling and Quade, 1993; Cerling et al., 1991; Cerling et al., 1992; Quade et al., 1989; Quade et al., 2007; Retallack, 2009; Solomon and Cerling, 1987).

In this chapter I first detail the governing equation and explain the basic method for estimating $p\text{CO}_2$ from the stable isotopes of pedogenic carbonates, which is essentially the same for all the chapters of this dissertation. The methods sections of those papers have been preserved as they were published (or submitted), but here I expand on the details, caveats, and pitfalls of using pedogenic carbonates to make reliable (at least, internally consistent) $p\text{CO}_2$ estimates. I also make a particular contribution to the methodology that, despite its apparent logic, has been overlooked by the community. I suggest how this contribution may ultimately help in determining the concentration of

respired CO₂ within a soil, a parameter that has often been overestimated (e.g, Ekart et al., 1999), and hence become a lightning rod for misinterpretation (e.g., Royer, 2010).

This section is by no means authoritative; rather, it is a ‘practicum’ in how the method can be applied efficiently to a large number of soils, particularly in drill core where detailed soil features are commonly difficult to recognize (many because they are larger than the lateral scale afforded by a typical <10 cm diameter core). I show how making good estimates is possible without relying upon apriori knowledge of a particular individual soil’s type or degree of development, removing uncertainty inherent to qualitative observational data.

2.2. The Pedogenic Carbonate Paleobarometer

In this section, I begin with the overall governing diffusion equation as a guide, and define the terms used in calculating a pCO₂ value. Each ensuing sub-section details the selection of variables, individual measurements, and assumptions that are considered for each parameter of the model.

2.2.1. The governing diffusion equation

Organic and inorganic carbon isotope measurements from individual paleosols are inputs into the soil diffusion model of Cerling (1999):

$$C_a = S(z) \frac{\delta_s - 1.0044\delta_\phi - 4.4}{\delta_a - \delta_s} \quad (\text{Eqn. 1})$$

where C_a is the concentration of atmospheric CO₂, $S(z)$ is the concentration of CO₂ at soil depths greater than 50cm contributed by the respiration of soil organic matter, δ_s is the $\delta^{13}\text{C}$ of soil CO₂, δ_ϕ is the $\delta^{13}\text{C}$ of soil-respired CO₂, and δ_a is the $\delta^{13}\text{C}$ of atmospheric

CO₂. All $\delta^{13}\text{C}$ values are relative to Vienna PeeDee Belemnite (VPDB). The 4.4 ‰ diffusion coefficient in the numerator of Eqn. 1 is due to the isotopic fractionation of $^{12}\text{CO}_2$ vs. $^{13}\text{CO}_2$ when diffusing through air.

2.2.2. Soil CO₂ and the effects of temperature on calcite precipitation

The carbon isotope ratio of soil CO₂ (δ_s) is a function of the mixing between the atmospheric CO₂ reservoir and the soil-respired reservoir at depth in the soil, and therefore carbonate nodules grow from this mixed soil-gas reservoir. For this reason, the carbon isotopic ratio of soil carbonate (δ_{cc}) is used as a proxy for the isotope ratio of the soil CO₂ (δ_s). The precipitation of calcite involves a temperature-dependent equilibrium fractionation between CaCO₃ and CO₂, which is described by:

$$10^3 \ln \alpha = 11.709 - 0.116(T) + 2.16 \times 10^{-4} (T)^2 \quad (\text{Eqn. 2})$$

where α is the fractionation factor, and T is temperature (in °C) (Cerling, 1999). Other empirical fractionation equations exist for pure calcite precipitation from generic aqueous solution (Mook et al., 1974; Romanek et al., 1992), but Eqn. 2 is based on observations specifically from paleosols. In the Newark and Hartford basins examined in the ensuing chapters of this dissertation, temperature is fixed at 25°C, as is deemed appropriate for these tropical basins. However, varying temperature at $25 \pm 5^\circ\text{C}$ imparts a ± 250 ppm error to a pCO₂ estimate of nominally 2000 ppm.

2.2.3. $\delta^{13}\text{C}$ with depth in the soil profile

A flawed assumption permeating much of the older literature is that a pedogenic carbonate nodule from below 50 cm soil depth is in equilibrium with soil CO₂, and therefore representative of that particular profile (Cerling et al., 1991; Ekart et al., 1999; Quade et al., 1989; Royer et al., 2001). For example, Figure 2.1 shows down-profile

$\delta^{13}\text{C}$ of pedogenic carbonates from soils used in Chapters 4 and 5, compared to the results of the diffusion model at steady state for atmospheric pCO_2 concentrations of 2000 and 4000 ppm. In the case of soil HPFD19T, a nodule from 50 cm depth gives a pCO_2 value that is as much as 2000 ppm higher than one selected from 100 or 120 cm depth (Fig. 2.1); if samples from 50 cm soil depth are deemed sufficient in each case, then pCO_2 would repeatedly be grossly overestimated (often by 1000's of ppm).

However, I can use a natural feature of soil carbonate precipitation to avoid this issue. The $\delta^{13}\text{C}$ value of pedogenic carbonate is known to decrease predictably with soil depth (Quade et al., 1989), and characterizing this trend makes it possible to differentiate between the relative influences of the atmospheric vs. soil-respired CO_2 reservoirs. Therefore, multiple (at least 5) down profile isotopic measurements are made on each paleosol to identify an equilibrium δ_{cc} value with depth in the soil (Schaller et al., 2011) (Fig. 2.1). Using only the mean of these depth-controlled measurements ensures that the mixing between the atmospheric and soil-respired reservoirs is at equilibrium with respect to the diffusion model, removing significant uncertainty in the isotopic maturity of a given paleosol profile.

This simple modification of the technique has greatly improved the precision of the estimates made in this study, and I recommend that any estimate in the literature made on the value of a single carbonate nodule assumed to be >50 cm depth should be rejected.

2.2.4. $\delta^{13}\text{C}$ of atmospheric CO_2 estimated from the $\delta^{13}\text{C}$ of soil organic matter

Because there is no carbon isotope fractionation due to respiration of organic matter, δ_ϕ is related directly to the carbon isotopic ratio of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$)

(Montanez et al., 2007). Therefore $\delta^{13}\text{C}_{\text{org}}$ is measured for each soil used in this study (see section 2.2.6 on avoiding diagenesis for details). The carbon isotopic ratio of the atmosphere is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by the following relationship (Arens et al., 2000):

$$\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10 \quad (\text{Eqn. 3})$$

which assumes consistent fractionation by photosynthesis. This assumption has the advantage of building any potential carbon cycle perturbations directly into the model, but ignores the myriad of physiologic and environmental effects that plants may impart on the $\delta^{13}\text{C}$ of organic tissues (e.g., Farquhar et al., 1989; Farquhar and Richards, 1984).

2.2.5. The concentration of respired CO_2 in the soil (the lightening rod)

The only truly adjustable parameter of the model is the concentration of CO_2 in the soil derived from the respiration of organic matter ($S(z)$), which is a product of soil productivity. This parameter is itself a function of several soil characteristics (such as soil permeability, free-air tortuosity, depth to characteristic CO_2 production, etc.), but none of these individual characteristics can be estimated from an ancient soil with any confidence because of the diagenetic conversion of soil to paleosol. For this reason, $S(z)$ is parameterized either qualitatively, or by empirical relationships based on observations from modern soils (Breecker et al., 2009a; Breecker et al., 2009b; Retallack, 2009).

Because empirical relationships can be used to systematically quantify a parameter, it is my preference to rely on those approaches for a first-order assessment. While most of the parameters used in Eqn. 1 are estimates of mean annual soil-forming conditions, recent findings from modern systems have demonstrated that pedogenic

carbonates precipitate during the driest times of the annual cycle, when soil productivity is likely to be substantially lower (Breecker et al., 2009a). Breecker used Monte Carlo simulations on the variables in Eqn. 1 to approximate the ratios of atmospheric $p\text{CO}_2$ to $S(z)$ values that produced the least amount of error, and found that when atmospheric $p\text{CO}_2/S(z)$ is between the values of 0.3 and 1.8, the estimation of atmospheric $p\text{CO}_2$ is most accurate. Results from down-profile studies of modern soils (Breecker et al., 2009a) indicate that $S(z)$ values closer to 2000 ppm are more accurate than the ~5000 ppm (4000-6000 ppm) typically assumed (e.g., Ekart et al., 1999; Montanez et al., 2007; Nordt et al., 2003). However, this does not help us quantitatively approximate the actual $S(z)$ value that should be used based on some measureable property of the soil.

Retallack (2009) suggests that the concentration of respired CO_2 is predictably related to the depth of the thick carbonate horizon in a given soil (depth to Bk, or 'D_s'). Retallack (2009) provides the following empirical relationship based on modern soils (Retallack, 2005):

$$S(z) = 66.7D_s + 588 \quad (\text{Eqn. 4})$$

This relationship works well (empirical standard error of $SE = \pm 893$ ppm) because of the correspondence between depth to Bk horizon and the mean annual precipitation received by a soil (Retallack, 2005; Royer, 1999), and by necessity, the correspondence between the productivity of a given soil and the amount of precipitation it receives. How this can be adjusted for the bias of seasonal drying, which is the time of pedogenic calcite precipitation occurs, has not yet been addressed (but see section 2.3, below).

The paleosols sampled in this study were relatively productive argillic and vertic calcisols (Mack et al., 1993). These soils have a mean depth to the carbonate (or Bk)

horizon (D_s) at 40 ± 15 cm soil depth (in this case, for the Hartford basin), which I use to estimate $S(z)$ by the empirical relationship in Eqn. 4: $S(z) = 66.7D_s + 588$ (Retallack, 2009). This results in a mean $S(z)$ of ~ 3256 with the compulsory standard error or SE of ± 893 ppm. Given the difficulty inherent in accurately estimating depth to the Bk horizon in individual paleosols from drill cores, and in accordance with the work of Breecker et al. (2009a, 2010), I use an $S(z)$ value of 3000 ± 1000 ppm for all pCO_2 estimates in this study. This value gives a final pCO_2 range that is indistinguishable from the error that would result from systematic use of the empirical depth to carbonate relationship on each and every paleosol. Individual soil profiles are not decompacted (as per Retallack, 2009), and our $S(z)$ approximations are therefore conservatively low because decompaction would increase D_s .

2.2.6. Ruling out the effects of diagenesis and other practical concerns

Figure 2.2 shows a particularly well-developed paleosol profile from the Pebble Bluff locality in the western Newark basin, which exposes part of the Perkasio member of the Passaic Formation (Sample locality NPPB1 in Chapter 5), and Figure 2.4 shows a thin section photomicrograph of a carbonate nodule from this profile. Characteristic features of pedogenesis (such as soil slickensides, accumulation of illuviated clays, etc. (Retallack, 2001)) are easily identified where the lateral exposure of a paleosol is large, such as in NPPB1 from Pebble Bluff (Fig. 2.2). This is in stark contrast to the lateral extent afforded by <10 cm diameter drill cores (Fig. 2.3), which have a lateral scale of the same order (and often much smaller) than many soil features. Therefore, below I list

some tricks that are handy when attempting to distinguish diagenetic, or non-pedogenetic signals in bulk soil carbonate isotope records.

A combination of thin sections and polished slabs are used to distinguish primary micritic calcite from diagenetic material (Driese and Mora, 2002) (see Fig. 2.4), with a sampling preference for small, isolated carbonate nodules (Fig. 2.5) that are generally in better isotopic equilibrium with the surrounding soil than larger nodules or calcretes (Schaller et al., 2011). Figures 2.4 and 2.5 show the distinction between primary micritic calcite due to pedogenesis, and secondary calcite microspar precipitates typical of diagenesis. Great care is taken to avoid phreatic calcretes, and to sample only those pedogenic carbonates displaying clear evidence of having formed in the vadose zone (Rasbury et al., 2006). If there is any groundwater influence, the original stable isotope signature due to pedogenesis is overprinted and the natural variability in $\delta^{13}\text{C}$ of pedogenic carbonate is minimized, showing very little change through the entire profile and no characteristic exponential decrease with depth. I reject these data points, which are common in soils formed where the precession index is high and soils probably became saturated while pedogenesis was still active.

Samples for organic carbon isotope analysis are taken from as close to the soil-surface as possible to avoid measuring recalcitrant organics unrelated to the active organic carbon pool during soil formation (Nadelhoffer and Fry, 1988). Also, several samples from each profile are homogenized to provide an organic carbon value that is most representative of the active respired pool during pedogenesis.

In the case of Chapter 3, where I estimate atmospheric pCO_2 concentrations directly before and after the eruption of the CAMP basalts, it should be noted that the

timescale of soil formation is on the order of several hundreds to thousands of years (Retallack, 2001). However, the timescale of basalt-flow cooling is probably something on the order of 10 to 100 years (e.g., Long and Wood, 1986), and hence, the flows themselves should be cooled and no longer degassing by at least 100-years post-extrusion. Therefore, the $p\text{CO}_2$ estimates made directly on top of the basalts should be representative of global atmospheric $p\text{CO}_2$ concentration, and not some local effect due to the basalts themselves. I discuss this further in section 6.3.

2.3. How can $S(z)$ be better estimated in the paleo-record?

In this section I briefly explore a refinement for the estimation of $S(z)$, based on the character of the down-profile $\delta^{13}\text{C}$ of individual soils, that I hope to complete in the future. I proceed under the working hypothesis that the change in $\delta^{13}\text{C}$ of pedogenic carbonate with soil depth is actually a function of the concentration of respired CO_2 in the soil (Quade et al., 1989).

All other factors being equal, including the concentration of CO_2 in the atmosphere, varying the concentration of respired CO_2 in a soil will change the down-profile isotopic composition of total soil CO_2 (see Fig. 2.6). As a matter of course, changing the level of productivity in a particular soil imparts the same effect, such that the carbon isotopic composition of soil CO_2 becomes asymptotic at an equilibrium isotopic value at a relatively shallow depth in high-productivity soils (Quade et al., 1989). Conversely, lower productivity soils reach equilibrium $\delta^{13}\text{C}$ values at a much greater depth in the soil. Lowering the soil productivity changes the characteristic depth

of CO₂ production by respiration, and also increases the depth to which atmospheric pCO₂ may penetrate a soil profile.

Because this $\delta^{13}\text{C}$ depth-function is also effected by the rate of any continuing sediment accumulation on a soil (Quade et al., 2007), we are left with two possible options to change the character of the $\delta^{13}\text{C}$ -depth function (at constant atmospheric pCO₂): differences in the concentration of respired CO₂ between the soils, or differences in the accretion rate on top of the active soil. Therefore, any estimates made using $\delta^{13}\text{C}$ -equilibrium depth functions must ensure there is no accumulation on the soil surface during pedogenesis.

Closer inspection of the individual sample sites in Figure 2.1 reveals that different soils reach equilibrium $\delta^{13}\text{C}$ values at vastly different depths. If dry-season soil-respired CO₂ concentrations may be related to total soil productivity, then this difference in character $\delta^{13}\text{C}$ -depth profile can be used to distinguish those soils that should be assigned a higher S(z) value from those that should have lower S(z). For example, higher productivity soil HNH2H2 equilibrates at a much shallower depth than lower productivity soil HPFD19T (Fig. 2.1).

The challenge then becomes one of calibration, and the next step is to calibrate the $\delta^{13}\text{C}$ -depth profile function in the modern, based on observations of soil CO₂ concentrations and isotopic composition using soil gas wells. If that were successful, I could derive a set of transfer functions that first describe the $\delta^{13}\text{C}$ -depth profile, and then relate this function to an effective S(z) value. Once calibrated, these transfer functions could predict the S(z) value most applicable to a $\delta^{13}\text{C}$ -depth profile from a paleosol,

hopefully resulting in a much more accurate estimate of paleo-pCO₂. This is a direction of significant future work.

2.4. References

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2.5. Figures and Captions

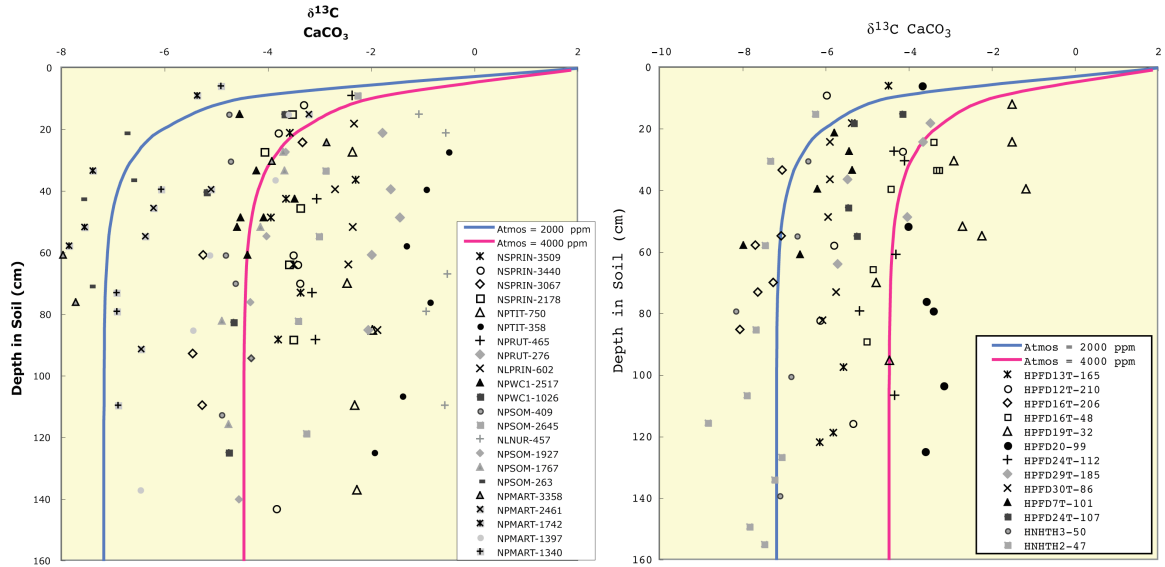


Figure 2.1: Down-profile $\delta^{13}\text{C}$ of pedogenic carbonates from soils used in Chapters 5 (a), from the Newark basin; and Chapter 4 (b), from the Hartford basin, compared to the results of the diffusion model at steady state for atmospheric $p\text{CO}_2$ concentrations of 2000 and 4000 ppm. Note that these sample depths correspond to the soil depths of sampled nodules, and not necessarily the depths to the Bk horizon needed to calculate $S(z)$ (Retallack, 2009). For this demonstration only, atmospheric $\delta^{13}\text{CO}_2$ was set to -6.5‰ , soil $\delta^{13}\text{C}_{\text{org}}$ was set to -26.5 , with an exponential production function and characteristic depth of production at 15 cm (other parameters described in text). For all $p\text{CO}_2$ estimates made in this study, the $\delta^{13}\text{C}_{\text{org}}$ was measured directly and used as a model input. Note that stabilization of measured δ_{cc} is commonly well below 50cm soil depth. Only the mean of the equilibrium δ_{cc} values were used to calculate $p\text{CO}_2$ in this study.



Figure 2.2: A particularly well-developed pedogenic carbonate bearing paleosol profile from the Pebble Bluff locality in the western Newark basin, which exposes part of the Perkasio member of the Passaic Formation (sample locality NPPB1 in Chapter 5). The horizontal white features are pedogenic carbonates that have accreted together for long enough to make a thick calcrete horizon (or Bk horizon), and the vertical features are carbonate rhizoliths typically formed around roots during pedogenesis. This profile shows a degree of carbonate development consistent with Gile's level III to IV (Gile et al., 1966). Hammer is ~25 cm long. Figure 2.4 shows a thin-section photomicrograph of a carbonate nodule from this profile.



Figure 2.3: Examples of well-developed nodular pedogenic carbonate horizons from the Stockton Formation, found at 1897 feet (A) and 1655.5 feet (B) in the NBCP Princeton core (See Chapter 5 for details). The lighter colored nodular features are pedogenic carbonates (arrows). Note difficulty in distinguishing many of the primary features of pedogenesis (such as the horizontal distribution of vertical rhizoliths) compared to those shown in Figure 2.2, despite similar levels of development (both at Gile's level III to IV (Gile et al., 1966)).

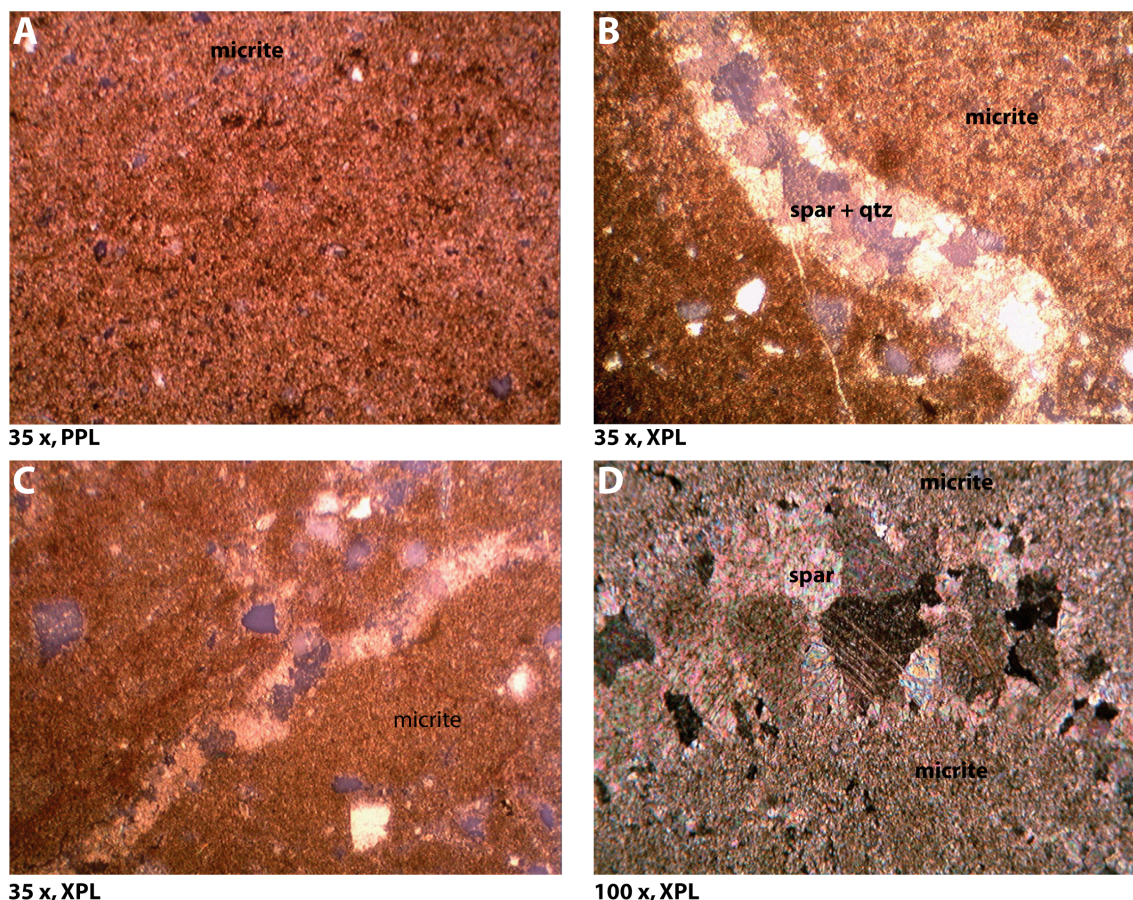


Figure 2.4: Photomicrographs of thin sections from various soils used in this study, which show the morphological distinction between primary micritic carbonate and diagenetic recrystallization of microspar (see Chapters 3, 4 and 5 for details on individual sample locations). Numbers preceding “x” indicate magnification, PPL = Plane polarized light, XPL = Crossed polarized light. **A.** Sample NSPRIN-2188: Clean micritic soil carbonate with no evidence of coarser-grained calcite microspar recrystallization. This sample has seen minimal diagenetic overprinting and retains micritic fabric typical of primary pedogenic carbonate precipitation. **B.** Sample HPFD24T-92.8: Secondary growth vein of quartz and calcite spar recrystallized through micritic carbonate nodule. **C.** Sample HPFD24T-80: Micritic calcite (fine-grained, brown), cut by secondary diagenetic growth vein of coarse calcite spar (pink) with minor quartz infilling (extinct at center). Proper sampling for stable isotope analysis would avoid these secondary diagenetic features and focus on the primary micritic calcite. **D.** Sample NPPB1: Detail of twinned coarse-grained calcite spar crystals infilling cracks in primary micritic carbonate.

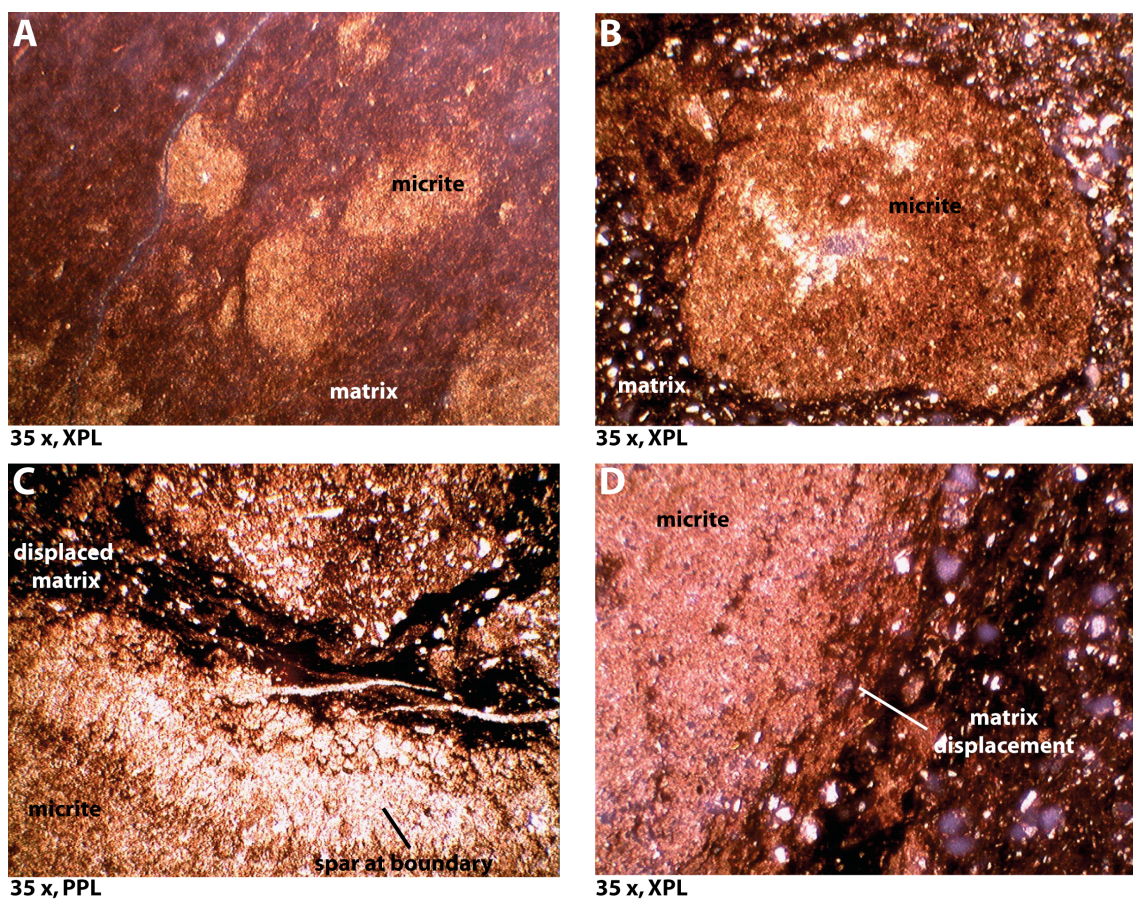


Figure 2.5: Photomicrographs of thin sections from various soils used in this study, which show the morphology of smaller, isolated micritic pedogenic carbonate nodules (those generally in best isotopic equilibrium with soil CO_2) in the context of their formation matrix. Numbers preceding “x” indicate magnification, PPL = Plane polarized light, XPL = Crossed polarized light. **A.** Sample HPFD30T-175.2: Isolated micritic nodules in arkosic soil matrix. **B.** Sample HPFJAI: Micritic nodule showing septarian fracture filled with microspar, in coarse quartz/feldspar sand matrix with hematite cement. **C.** Sample NSPRIN-2188: Displacive micritic carbonate growing against quartz sand soil matrix. Note accumulation of hematite cement and clay at nodule boundary, with coarse spar recrystallization of micrite along edge of nodule. **D.** Sample NFPT26-246.9: Samples from ACE-core PT-26, which covers the top of the Orange Mountain Basalt and basal Feltville formation in the Newark Basin. Micritic calcite precipitated in soil matrix, displacing arkosic (quartz, feldspar) matrix with significant hematite cement.

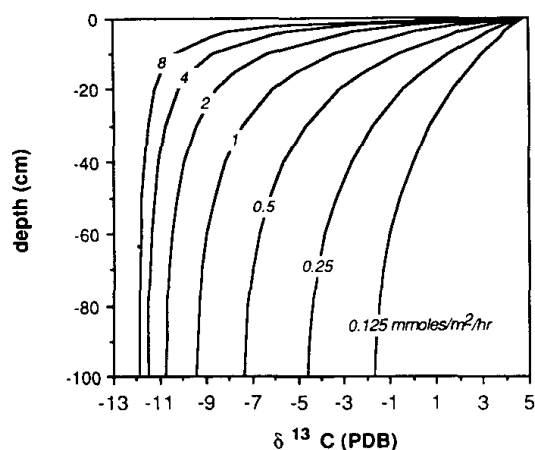


Figure 2. Isotopic composition of pedogenic carbonates calculated from soil CO₂ model described in text for 1 atm pressure, $T = 15\text{ }^{\circ}\text{C}$, $\epsilon = 0.5$, $\delta^{13}\text{C}$ (respired CO₂) = $\delta\theta = -27$ per mil, and $\delta^{13}\text{C}$ (atmospheric) = $\delta\alpha = -6$ per mil at 300 ppmV.

Figure 2.6: the $\delta^{13}\text{C}$ of soil CO₂-based prediction of the $\delta^{13}\text{C}$ of pedogenic carbonates with depth in the soil for a number of different soil productivity scenarios (taken from Quade et al. (1989)). Original caption of Quade et al. (1989) reproduced to show model constraints.

Chapter 3

Atmospheric $p\text{CO}_2$ perturbations associated with the Central Atlantic Magmatic Province¹

3.1. Abstract

The effects of a large igneous province on the concentration of atmospheric carbon dioxide ($p\text{CO}_2$) are mostly unknown. In this study we estimate $p\text{CO}_2$ from stable isotopic values of pedogenic carbonates interbedded with volcanics of the Central Atlantic Magmatic Province (CAMP) in the Newark basin, eastern North America. We find pre-CAMP $p\text{CO}_2$ values of ~2000 parts per million (ppm), increasing to ~4400 ppm immediately after the first volcanic unit, followed by a steady decrease toward pre-eruptive levels over the subsequent 300 thousand years, a pattern that is repeated after the second and third flow units. We interpret each $p\text{CO}_2$ increase as a direct response to magmatic activity (primary outgassing or contact metamorphism). The systematic decreases in $p\text{CO}_2$ following each magmatic episode probably reflect consumption of atmospheric CO_2 by weathering of silicates, stimulated by fresh CAMP volcanics.

3.2. Introduction

Large igneous provinces (LIPs) are geologically rapid episodes of extensive volcanism, often flooding vast oceanic or continental regions with several million cubic kilometers of lava (Coffin and Eldholm, 1993). In particular, continental flood basalts have the potential to directly perturb Earth's climate system through the emission of

¹ Schaller, M. F., Wright, J. D., and Kent, D. V., 2011, Atmospheric $p\text{CO}_2$ Perturbations Associated with the Central Atlantic Magmatic Province: *Science*, v. 331, no. 6023, p. 1404-1409.

gasses to the atmosphere, most notably, SO₂ and CO₂, which together may result in an immediate (1 – 10 year) cooling (Pollack et al., 1976; Rampino et al., 1985), followed by a longer-term (10² – 10⁵ year) warming (Hansen et al., 2008). Of these, only CO₂ has the potential to influence climate on both short- and long-timescales because of its relatively long atmospheric residence time and effectiveness as a greenhouse gas, leading some to conclude that CO₂ is the primary driver of Phanerozoic climate (Royer et al., 2004).

If the concentration of atmospheric CO₂ exerts an influence on climate over such broad timescales, what are the effects of a LIP on this essential parameter of the carbon cycle? Although the potential radiative effects of LIP CO₂ degassing on the million-year scale have been considered inconsequential (Caldeira and Rampino, 1990; Self et al., 2006), shorter (10⁴-10⁵ year) timescale reconstructions of atmospheric partial pressure of CO₂ (*p*CO₂) before and after LIP eruptions have not been systematically determined because of inadequate chronostratigraphic resolution in most settings (e.g., Cleveland et al., 2008; McElwain et al., 1999). Consequently, the direct *p*CO₂ effect of a LIP remains untested empirically.

Intriguingly, LIP volcanism is often temporally associated with mass extinction events throughout Earth History (Wignall, 2001). The three largest continental LIPs of the Phanerozoic are the Siberian Traps, the Central Atlantic Magmatic Province (CAMP), and the Deccan Traps, each of which is linked to one of the “Big-5” Phanerozoic mass extinctions (the end-Permian, end-Triassic, and the Cretaceous–Paleogene events, respectively) (Courillot et al., 1999; Courillot and Renne, 2003). Though attempts have been made to estimate the gaseous emissions attributable to the Deccan (Beerling et al., 2002; Caldeira and Rampino, 1990; Nordt et al., 2002) and

Siberian (Grard et al., 2005; Svensen et al., 2009) traps, it is difficult to demonstrate causality because the uncertainties in correlating these $p\text{CO}_2$ estimates from afar to the volcanic stratigraphy itself is usually no better than the turnover time of an atmospheric $p\text{CO}_2$ perturbation (Dessert et al., 2001). Of these, only the CAMP is sequenced in high-resolution, temporally continuous sediments that contain paleosols appropriate for estimating $p\text{CO}_2$, and have a well-established chronology (Kent and Olsen, 1999; Olsen et al., 1996a) and extinction level.

Extrusives from the CAMP (Marzoli et al., 1999) are preserved in direct stratigraphic succession with cyclic continental sediments in the Newark basin of Eastern North America (Fig. 3.1). Milankovitch cyclostratigraphy of the primarily lacustrine sediments interbedded within the CAMP extrusives have yielded precise age control (to the level of orbital precession) and an estimated total volcanic duration of $\sim 600 \pm 20$ thousand years (ky) (Olsen et al., 2003; Olsen et al., 1996b). In this same Newark basin section, palynofloral evidence of the end-Triassic extinction (ETE) is found stratigraphically just below the first of the CAMP volcanics, preceding the magmatism by ~ 20 ky (Fowell et al., 1994; See Olsen et al., 2002 for review). Also interspersed throughout these sediments, and often forming from CAMP lava flows themselves, are pedogenic carbonate-bearing paleosols (see Fig. 3.2A and B) which can be used to estimate ancient atmospheric $p\text{CO}_2$ (Cerling, 1992). Thus, the Newark stratigraphy is ideally situated to directly test the $p\text{CO}_2$ effect of a LIP. Previous attempts at reconstructing the $p\text{CO}_2$ effect associated with CAMP extrusives had very sparse sampling resolution (Tanner et al., 2001) or had to rely on imprecise long-distance correlation (Cleveland et al., 2008; McElwain et al., 1999).

We use $\delta^{13}\text{C}$ measurements of pedogenic carbonate nodules from paleosols stratigraphically distributed before and after each extrusive unit to generate a high-resolution $p\text{CO}_2$ record through the Newark Basin CAMP sequence (Figure 1). The extrusion of $\sim 2 - 4 \times 10^6 \text{ km}^3$ of volcanics (Holbrook and Kelemen, 1993; McHone, 2003) in less than a million years implies a measurable effect on atmospheric $p\text{CO}_2$, which our temporal resolution should allow us to detect. According to the model of Dessert et al. (2001) scaled to the Deccan Traps, the transient increase in $p\text{CO}_2$ is on the time-scale of the eruptions, after which continental silicate weathering should lower $p\text{CO}_2$ to pre-eruption levels in $\sim 1 \text{ My}$.

3.3. Estimating $p\text{CO}_2$ from pedogenic carbonates

Organic and inorganic carbon isotope measurements on paleosols from outcrop, and from multiple, stratigraphically overlapping cores taken by the Army Corps of Engineers (ACE) through the extrusive interval (Fig. 3.S1), are used as inputs into the diffusion model of Cerling (1999):

$$C_a = S(z) \frac{\delta_s - 1.0044\delta_\phi - 4.4}{\delta_a - \delta_s}$$

where C_a is the concentration of atmospheric CO_2 , $S(z)$ is the concentration of CO_2 due to respiration of soil organic matter, δ_s is the $\delta^{13}\text{C}$ of soil CO_2 , δ_ϕ is the $\delta^{13}\text{C}$ of soil-respired CO_2 , and δ_a is the $\delta^{13}\text{C}$ of atmospheric CO_2 . All δ values are relative to Vienna PeeDee Belemnite (VPDB). The temperature of calcite precipitation is set at 25°C , relating the carbon isotopic ratio of soil carbonate (δ_{cc}) to δ_s . As an independent objective metric of soil applicability, multiple (at least three) down profile δ_{cc} measurements were made on

each paleosol to reproduce the expected exponential decrease toward stabilization with depth (Fig. 3.2, Quade et al., 1989). Using the mean of these soil-equilibrated measurements ensures that the mixing between the atmospheric and soil-respired reservoirs is at equilibrium with respect to the diffusion model. The measured carbon isotopic ratio of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$) is related directly to δ_ϕ . Carbon cycle perturbations are built into the model because the carbon isotopic ratio of the atmosphere (δ_a) is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by assuming consistent fractionation by photosynthesis: $\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10$ (Arens et al., 2000). We use an $S(z)$ value of 3000 ± 1000 parts per million (ppm), appropriate for soils developed in a semi-arid climate with moderate productivity (Breecker et al., 2009; Cerling, 1999).

3.4. Atmospheric $p\text{CO}_2$ estimates in superposition with CAMP basalts

Pedogenic carbonates from the upper Passaic Formation deposited before the first CAMP volcanic unit (Orange Mountain Basalt) have $\delta^{13}\text{C}$ values generally below -5‰ VPDB, with $\pm 1.5\text{‰}$ variability (Figure 1B). The carbon isotopic composition of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$) is remarkably stable around -26‰ (Fig. 3.1C), consistent with but less variable overall than results from independent analyses of wood and total organic carbon from elsewhere in the Newark and Hartford stratigraphy (Whiteside et al., 2010). Model results of the pedogenic carbonate paleobarometer yield $p\text{CO}_2$ estimates with a mean of ~ 2000 ppm ($S(z) = 3000$ ppm) in the pre-CAMP stratigraphy (Fig. 3.1D). These estimates from over 500 m of the uppermost Passaic Formation, deposited over ~ 2.5 Myr of the latest Triassic (Kent and Olsen, 1999; Olsen et al., 1996a), show internal consistency between outcrop and between cores, and with the tight stratigraphic

resolution suggest that there are no major CO₂-producing magmatic events prior to the observed Orange Mountain Basalt. This stable $p\text{CO}_2$ background is probably a measure of equilibrium continental silicate weathering in the Late Triassic.

The ~2000 ppm pre-CAMP $p\text{CO}_2$ baseline found in this study is not inconsistent with widely (geographically and stratigraphically) dispersed pedogenic carbonate estimates from elsewhere in the Newark Supergroup (Suchecki et al., 1988; Tanner et al., 2001) or reconstructions from the Late Triassic Petrified Forest section (Cleveland et al., 2008) (Fig. 3.3). However, the Petrified Forest section lacks CAMP volcanics and can be correlated to the Newark succession only at the stage level (Cleveland et al., 2007), in which case the Rhaetian samples most likely overlap with the 2.5 Myr (Kent and Olsen, 1999) pre-CAMP samples of this study but show considerably greater variability (500 to 3500 ppm; Fig. 3.3). The high variability in the Petrified Forest section is probably due to the lack of down-profile isotope measurements and the use of temperatures estimated from the $\delta^{18}\text{O}$ of pedogenic calcite, which lacks a reliable calibration for use in the paleo-record (Dworkin et al., 2005).

The carbon isotope value of pedogenic carbonate formed directly on top of the Orange Mountain Basalt (first flow unit) is enriched in ^{13}C by 1-2‰ above the pre-CAMP background (Fig. 3.1B). This increase, and similar increases above the Preakness and Hook Mountain basalts (the second and third flow units, respectively) reflect the increased influence of the atmospheric reservoir on soil carbonate formed at depth. Stratigraphically above each flow unit the carbon isotope composition of soil organic matter decreases by ~0.5 to 1.0 ‰, followed by a general return of $\delta^{13}\text{C}_{\text{org}}$ values to around -26‰, but with increased variability (Fig. 3.1C). The $\delta^{13}\text{C}$ values of pedogenic

carbonate and soil organic matter directly above the Preakness Basalt have particularly good reproducibility between several laterally equivalent individual cored sections, allowing confidence in these measurements. Those soils formed on top of the Orange Mountain Basalt (Fig. 3.2B) show an increase in $p\text{CO}_2$ to 4400 ppm (Fig. 3.1D), which amounts to a doubling of $p\text{CO}_2$ above the pre-CAMP baseline. In every case, pedogenic carbonate samples of soils formed on the tops of the basaltic units yield $p\text{CO}_2$ estimates that are distinctly higher than the immediately pre-eruptive background levels (Fig. 3.1): 4200 ppm on top of the Preakness Basalt compared with 3000 ppm in the uppermost portion of the underlying Feltville Formation, and 5000 ppm directly on the Hook Mountain Basalt compared with 2500 ppm in the uppermost portion of the underlying Towaco Formation. This pattern suggests that the volcanism associated with each lava flow unit had a direct effect on atmospheric $p\text{CO}_2$ by ~ 2000 ppm, and was virtually immediate (to within the resolution of orbital precession (~ 20 kyr)).

3.5. Chronostratigraphic control of $p\text{CO}_2$ estimates

A previous low resolution reconstruction from the Newark Supergroup (two localities over 10 My) seemed to suggest relatively stable $p\text{CO}_2$ levels across the CAMP interval (Tanner et al., 2001) and in comparison to our study, underscores the difficulty in attempting to capture a transient perturbation of the carbon system without adequate chronostratigraphic control (e.g., Beerling, 2002; Retallack, 2002) (Fig. 3.3). The stratigraphic level of the McCoy Brook sample of Tanner et al. (2001) from the Fundy Basin is not known precisely (e.g., Tanner, 2003) and it is quite possible that the soil formed long enough after emplacement of the North Mountain Basalt (correlative to the

Orange Mountain Basalt) (Whiteside et al., 2007) that the full $p\text{CO}_2$ increase was not recorded. As demonstrated by this study, capturing such a transient signal requires <100 kyr sampling resolution with respect to the volcanics. Other attempts to estimate $p\text{CO}_2$ over this interval, most notably the approximations using stomatal densities of leaf fossils from end-Triassic event boundary sections in Greenland and Sweden (McElwain et al., 1999), indicate a doubling to tripling of $p\text{CO}_2$ from 800 to 2100 ppm (Fig. 3.3). These stomata-based estimates are substantially lower than those found here, but the stomata proxy is thought to underestimate $p\text{CO}_2$ (Beerling and Royer, 2002), in which case a reported doubling to tripling broadly agrees with our findings and is corroborated by other cuticular estimates (Retallack, 2001).

If the increase in $p\text{CO}_2$ after each major basaltic unit (Orange Mountain, Preakness, and Hook Mountain Basalts) can be ascribed to episodes of magmatic activity, which are likely to be very short (Olsen et al., 1996b), then the relatively high resolution record of $p\text{CO}_2$ taken as a whole seems to require just the three distinct episodes of volcanism. This does not necessarily imply that the local thicknesses of the CAMP volcanics in the Newark are representative of the global volume of basalt produced by each flow unit. For example, although the Newark and Hartford basins show three distinct volcanic episodes in nearly identical chronostratigraphic sequence (Olsen, 1988; Whiteside et al., 2007), the thicknesses of the correlative flow units vary by a factor of 2. Nonetheless, the observed magnitude and singularity of the $p\text{CO}_2$ response to each flow unit in the Newark implies that the magmatic events that produced them were regionally extensive and voluminous, because atmospheric CO_2 is globally homogeneous on the circulation time of the atmosphere. Although the second episode of

magmatism produced the thickest lava flow unit (Preakness Basalt) in the Newark basin, there is only a relatively small corollary increase in $p\text{CO}_2$. Interestingly, a middle flow unit equivalent to the Preakness Basalt is not present in the South Atlas region of Morocco, whereas the uppermost flow unit there (Recurrent Basalt) is stratigraphically and geochemically equivalent to the Hook Mountain Basalt in the Newark basin (Whiteside et al., 2007). Although the Hook Mountain Basalt is locally thin in the Newark, the associated $p\text{CO}_2$ increase is one of the largest recorded, implying that greater unrecorded volumes were erupted elsewhere. This body of evidence demonstrates the global applicability of the $p\text{CO}_2$ findings reported here; together, they make a compelling case that what has been recorded in the Newark basin is a reasonable representation of a global sequence of events.

To gauge the plausibility of a volcanic CO_2 source, we can compare the CO_2 efflux potential of the CAMP basalt volume to the effect observed in the Newark. Assuming a total CAMP volume of $2.4 \times 10^6 \text{ km}^3$ (McHone, 2003), and a volcanic efflux of $1.4 \times 10^{10} \text{ kg of CO}_2 \text{ per km}^3$ (Self et al., 2006), we estimate a total CO_2 degassing potential of $3.36 \times 10^{16} \text{ kg CO}_2$. We focus on the lower volcanic unit (represented by the Orange Mountain Basalt in the Newark basin) for which the pre-eruption background $p\text{CO}_2$ is well established. That initial pulse of activity represents roughly one-third of the total CAMP volume, and therefore could have produced $1.12 \times 10^{16} \text{ kg of CO}_2$, amounting to a $\sim 1400 \text{ ppm}$ increase in $p\text{CO}_2$ (at $7.82 \times 10^{12} \text{ kg CO}_2 \text{ per ppm}$). This instantaneous approximation is of the same order and within the error of our observed $\sim 2000 \text{ ppm}$ $p\text{CO}_2$ increase after the first major episode of CAMP volcanism, implying that the volcanic release of CO_2 was extremely rapid, which is consistent with

the sporadic presence of only very thin and discontinuous sedimentary strata between flows (Olsen et al., 2003; Whiteside et al., 2007). However, this does not preclude that a major component of the observed $p\text{CO}_2$ increase is contact metamorphic in origin (e.g., Svensen et al., 2004), which is hinted at by the small decrease in $\delta^{13}\text{C}_{\text{OM}}$ above each flow unit.

3.6. The influence of basalt weathering

An intriguing phenomenon recorded by the Newark basin paleosol sequence is the gradual apparent decrease in $p\text{CO}_2$ over time scales of 10^5 -year after each successive episode of volcanism (Fig. 3.4). For example, elevated $p\text{CO}_2$ values just after the Preakness Basalt in the ~300 kyr-long Towaco Formation have nearly returned to pre-eruptive levels by the emplacement of the succeeding Hook Mountain Basalt. We attribute the systematic decrease in $p\text{CO}_2$ as the enhanced response of continental silicate weathering consuming each volcanic input of CO_2 (Walker et al., 1981). Given the vast aerial extent of CAMP extrusive activity (McHone, 2003), it is plausible to attribute the rapidity of the decrease in atmospheric CO_2 to consumption by hydrolysis of the CAMP volcanics themselves, especially in the tropical humid belt where the engines of continental weathering are most effective (Dessert et al., 2003). Geochemical modeling of the period after emplacement of the Deccan LIP and its corresponding CO_2 input show a similar exponential decrease in $p\text{CO}_2$ due to consumption by weathering (Dessert et al., 2001) (Fig. 3.4). Marine osmium isotope evidence also indicates that an increase in continental weathering followed the CAMP interval (Cohen and Coe, 2007), lending credibility to a weathering hypothesis. Though the CAMP data correspond well to the

initial stages of this modeled decrease, the uppermost portion of the Newark basin section is truncated, so the full extent of this relationship cannot be evaluated here.

3.7. Implications for the End-Triassic Extinction

Neither the Feltville nor Towaco formations show evidence of $p\text{CO}_2$ changes that can be associated with magmatic events other than those directly related to the observed volcanics. Similarly, the stability of $p\text{CO}_2$ estimates in the Pre-CAMP Passaic Fm. leaves the ETE without an obvious $p\text{CO}_2$ precursor. However, the youngest sample in the pre-extrusive section (Exeter Member, Fig. 3.1) formed in a soil pre-dating the first flow unit by only ~20 kyrs. This soil occurs two meters below the clay layer containing palynofloral evidence for the ETE in the same exposure, which itself predates the observed onset of volcanism in the Newark by ~19 ky (Olsen et al., 2002). At these sedimentation rates, the uppermost paleosol sample that we studied in the Newark probably pre-dates the ETE by perhaps as little as ~1 kyr. Therefore, it is possible that a pulse of CAMP volcanism and an attendant rapid rise in atmospheric $p\text{CO}_2$ with associated climatic implications occurred within the ~20 ky paleosol sampling gap before the age-equivalent of the Orange Mountain Basalt but remains undocumented. Nonetheless, the tight stratigraphic constraint implies that whatever phenomenon caused the ETE must have been very abrupt (occurring within a narrow thousand year window), or have had minimal effect on atmospheric $p\text{CO}_2$ if it occurred earlier.

several meters below the equivalent of the Orange Mountain Basalt (OMB, the first flow unit) in the Jacksonwald section of the Newark Basin (Olsen et al., 2002). Stratigraphic thickness is scaled arbitrarily from the base of the laterally extensive OMB. **B.** Profile equilibrated mean $\delta^{13}\text{C}$ values of pedogenic carbonate in the Newark stratigraphic section, error is $\pm$ SD of mean (See Table S1 and Fig. 3.2). Circular symbols are samples from core, squares are outcrop. **C.** Measured $\delta^{13}\text{C}$ values of preserved soil organic matter from clay linings or as close to the paleosol surface as possible. **D.** The results of the pedogenic carbonate paleobarometer based on the input variables from B and C at 25°C. The concentration of respired CO_2 in the soil ($S(z)$) was estimated to be 3000 ± 1000 ppm (error bars), corresponding to a plausible range for mid-productivity tropical soils and likely encompassing the range of calculated atmospheric $p\text{CO}_2$ values. Carbon cycle perturbations are built into the model because the carbon isotopic ratio of the atmosphere (δ_a) is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by: $\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10$ (Arens et al., 2000), which assumes consistent fractionation by photosynthesis (See Chapter 3S, and Table 3.S1 for numerical values).

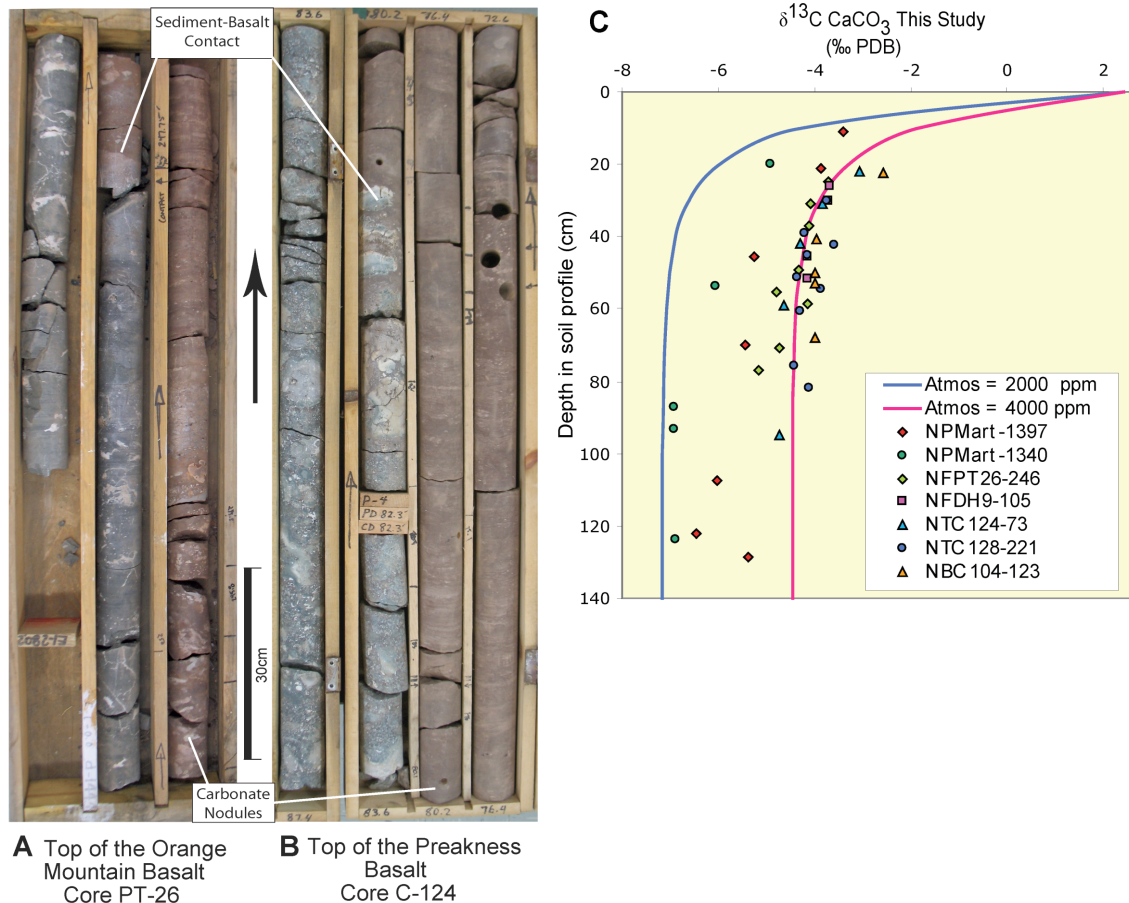


Figure 3.2: Carbonate bearing calcic vertisols formed directly on the tops of the lava flows; **(A)** on top of the Orange Mountain Basalt in ACE core PT-26, Box 18; and **(B)** on top of the Preakness Basalt in ACE core C-124, Box 3 (see Fig. 3.1 for stratigraphic column, Fig. 3.S1 for core locations). Scale bar is 30cm, depth in core decreases from Left (deepest) to Right (shallowest), up-core direction is indicated by arrow, holes are

soil carbonate sampling locations. Such superposition removes any stratigraphic uncertainty from these $p\text{CO}_2$ estimates with regard to the flow units themselves. **C.** Down-soil $\delta^{13}\text{C}$ profiles of pedogenic carbonates (δ_{cc}) from representative paleosols in the Passaic, Feltville, Towaco and Boonton Formations used in this study (symbols, symbols encompass analytical error), compared to the δ_{cc} predicted by the diffusion model at atmospheric CO_2 concentrations of 2000 and 4000 ppm (blue and pink lines, respectively) (after Quade et al., 1989). For this exercise only, atmospheric $\delta^{13}\text{CO}_2$ was set to -6.5‰, soil $\delta^{13}\text{C}_{\text{org}}$ was set to -26.5, with an exponential production function and characteristic depth of production at 15cm (other parameters as described in (See Chapter 3S for description of other parameters); for all $p\text{CO}_2$ estimates made in this study, the $\delta^{13}\text{C}_{\text{org}}$ was measured directly and used as a model input. Soil carbonate above 20cm in the profile was rare, note that stabilization of measured δ_{cc} is often well below 50cm soil depth. Using the mean of these depth-stabilized measurements ensures that the mixing between the atmospheric and soil-respired reservoirs at equilibrium with respect to the diffusion model. Photographs of the soils used in C, from samples NFPT26 and NTC124, are shown in A and B.

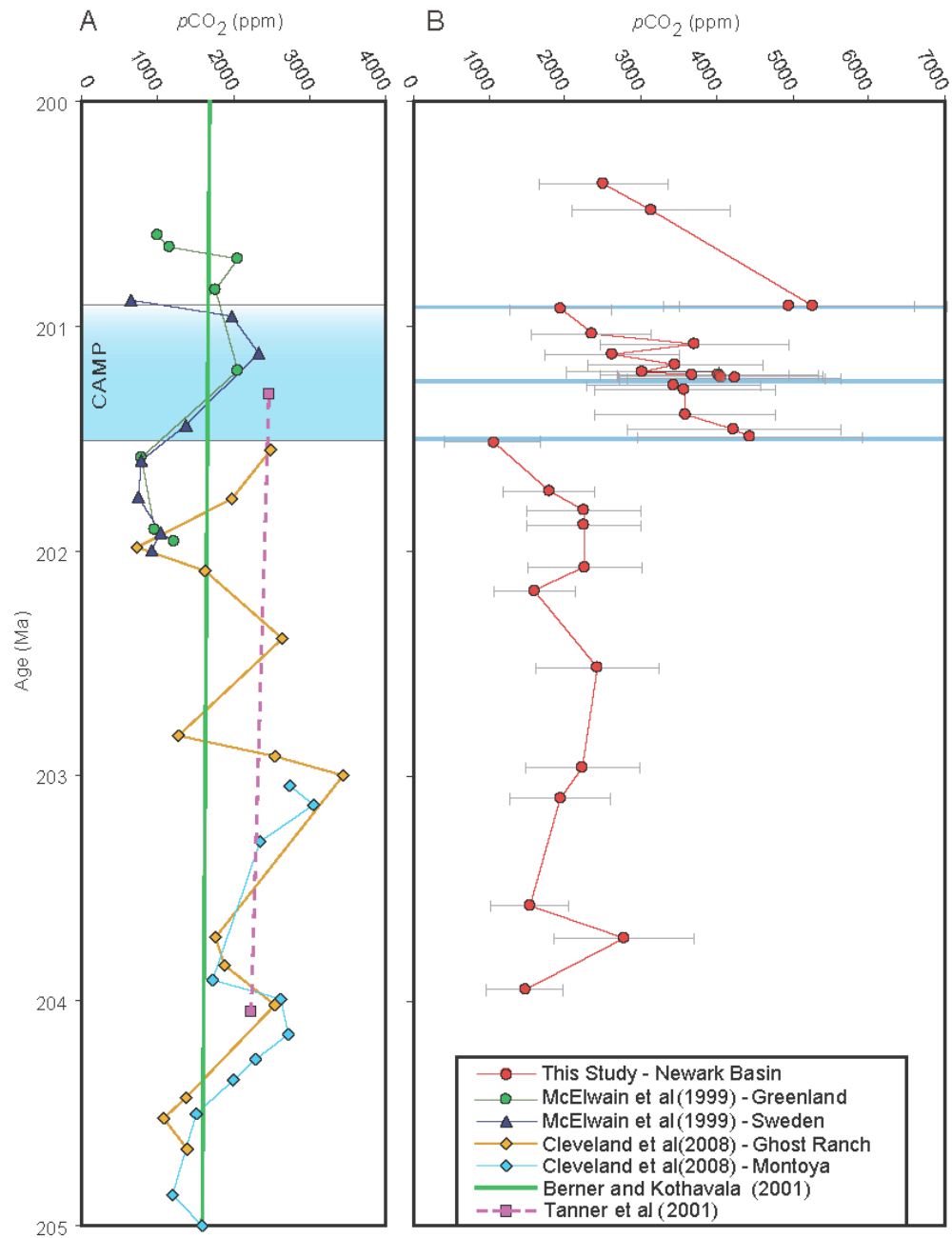


Figure 3.3: **A.** Atmospheric $p\text{CO}_2$ estimates previously made on Late Triassic and Early Jurassic sections using low resolution pedogenic carbonates from other basins in the Newark Group (Tanner et al., 2001) and the Rhaetian data of Cleveland et al from the Petrified Forest section (Cleveland et al., 2008); stomatal densities from sections in Greenland and Sweden (McElwain et al., 1999); and geochemical modeling (Berner and Kothavala, 2001). Approximate placement of the CAMP is shown in blue. The McElwain data were placed using the magnetic stratigraphy of Kent and Clemmensen (1996) and Whiteside et al. (Whiteside et al., 2010). **B.** $p\text{CO}_2$ estimates of this study with time (error bars are $S(z) = 3000 \pm 1000$ ppm). The samples taken in this study are from the same series of ACE cores used to construct a time sequence through the magmatic

interval in the Newark Basin (Olsen et al., 1996b). The heavy blue lines indicate the temporal placement (and duration) of each CAMP flow unit.

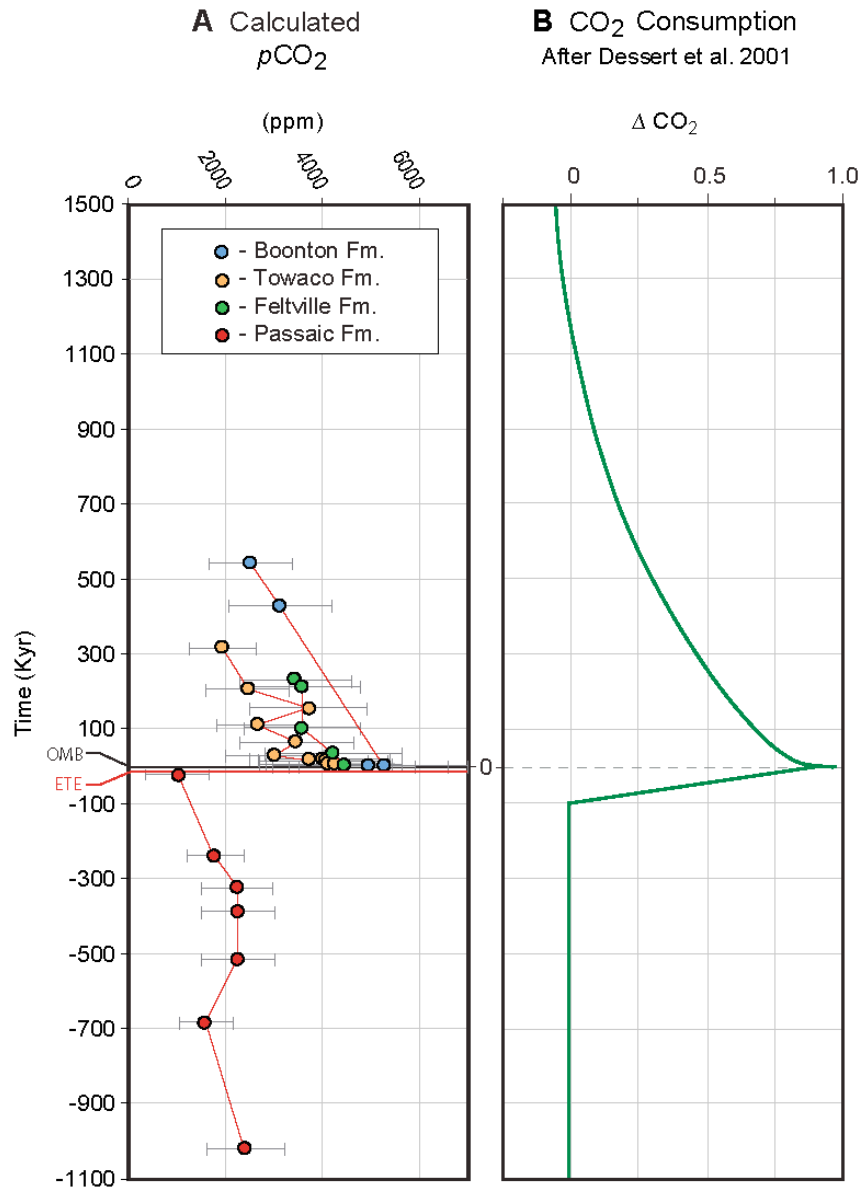


Figure 3.4: **A.** Calculated $p\text{CO}_2$ of this study vs. time relative to the top of the Orange Mountain Basalt in the Newark Basin (the first CAMP flow unit). The $p\text{CO}_2$ estimates following each successive flow unit in the Newark have been normalized to the initial extrusive event for comparison to a silicate weathering model (colored symbols, error bars are $S(z) = 3000 \pm 1000$ ppm). **B.** Modeled CO_2 consumption due to weathering (Dessert et al., 2001) after emplacement of the Deccan Traps. In the model, a pulse of CO_2 was added to the atmosphere (over 100 kyrs) accompanying the extrusion of the Deccan LIP. The change in $p\text{CO}_2$ represents the remaining fraction of the total $p\text{CO}_2$ increase in this particular modeling scenario. The abrupt increase of $p\text{CO}_2$ and subsequent post-extrusive drawdown found in response to the CAMP volcanism in this study (A) is remarkably similar to the modeling results of Dessert et al. (Dessert et al.,

2001), bearing in mind the much longer interval of igneous activity assumed in the model.

3.9. Supporting Online Material

3.9.1. Detailed Methodology

Pedogenic carbonate nodules were collected from paleosols located stratigraphically before and after each of the CAMP flows in the Newark Basin from both cores and outcrop. A series of short cores taken by the Army Corps of Engineers (ACE) covers the extrusive interval in high resolution (Fedosh and Smoot, 1988) (Fig. 3.S1), overlapping significantly with the Newark Basin Coring Project (NBCP) Martinsville core (Olsen et al., 1996a; Olsen et al., 1996b). Immediately above each CAMP flow unit, carbonate bearing calcic vertisols formed directly on the tops of the lava flows (e.g., see Figure 3.2A and B), removing any stratigraphic uncertainty from these pCO₂ estimates with regard to the flows themselves.

Organic and inorganic carbon isotope measurements from these paleosols were used as inputs into the diffusion model of Cerling (1999):

$$C_a = S(z) \frac{\delta_s - 1.0044\delta_\phi - 4.4}{\delta_a - \delta_s}$$

where C_a is the concentration of atmospheric CO₂, $S(z)$ is the concentration of CO₂ at soil depths greater than 50cm contributed by the respiration of soil organic matter throughout, δ_s is the $\delta^{13}\text{C}$ of soil CO₂, δ_ϕ is the $\delta^{13}\text{C}$ of soil-respired CO₂, and δ_a is the $\delta^{13}\text{C}$ of atmospheric CO₂. All δ values are relative to Vienna PeeDee Belemnite (VPDB).

The carbon isotopic ratio of soil carbonate (δ_{cc}) is used as a proxy for δ_s , which involves a temperature dependent equilibrium fractionation between CaCO₃ and CO₂, described by:

$$10^3 \ln \alpha = 11.709 - 0.116(T) + 2.16 \times 10^{-4} (T)^2 \quad (\text{Cerling, 1999})$$

where α is the fractionation factor, and temperature (T , in $^{\circ}\text{C}$) is fixed at 25°C , as is appropriate for the equatorial Newark Basin and consistent with previous work. Since respiration involves no carbon isotope discrimination, δ_{ϕ} is related directly to the carbon isotopic ratio of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$). Carbon cycle perturbations are built into the model because the carbon isotopic ratio of the atmosphere is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by the following relationship (Arens et al., 2000):

$$\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10$$

which assumes consistent fractionation by photosynthesis. The only significant adjustable parameter of the model is the concentration of CO_2 in the soil derived from the respiration of organic matter ($S(z)$), which is a function of soil productivity. We use an $S(z)$ value of 3000 ± 1000 ppm, appropriate for soils developed in a semi-arid climate with moderate productivity (Breecker et al., 2009; Cerling, 1999), and likely encompasses the plausible range of calculated atmospheric pCO_2 values.

Thin sections and polished slabs were used to identify primary micritic calcite from diagenetic material (Driese and Mora, 2002). Samples for carbon isotope ratio analysis of organic matter were taken from as close to the paleo-surface as possible, to avoid measuring recalcitrant organics unrelated to the active organic carbon pool during soil formation (Nadelhoffer and Fry, 1988).

The $\delta^{13}\text{C}$ value of pedogenic carbonate is known to decrease predictably with soil depth, making it possible to differentiate between the relative influences of the atmospheric vs. soil-respired CO_2 reservoirs by characterizing this trend. Accordingly, multiple (at least 3) down profile isotopic measurements were made on each paleosol to

reproduce the expected exponential decrease in δ_{cc} toward equilibrium with depth (Quade et al., 1989) (Figure 3.2). Using the mean of these depth-stabilized measurements ensures that the mixing between the atmospheric and soil respired reservoirs is at equilibrium with respect to the diffusion model, removing significant uncertainty in the isotopic maturity of a given paleosol profile. This method provides an independent metric of data quality where those soils that do not show predictable down-profile isotopic trends are rejected.

Chronostratigraphic placement was accomplished using the cyclostratigraphy Olsen et al. (Olsen et al., 1996b), based a subset of the same suite of ACE cores exploited more comprehensively by this study. This cyclostratigraphy provides direct stratigraphic age control to the level of the precession cycle, where the lava flow units themselves are determined to represent negligible amounts of time, with a complete eruptive duration of 600 ± 20 kyrs (Olsen et al., 2003; Olsen et al., 1996b).

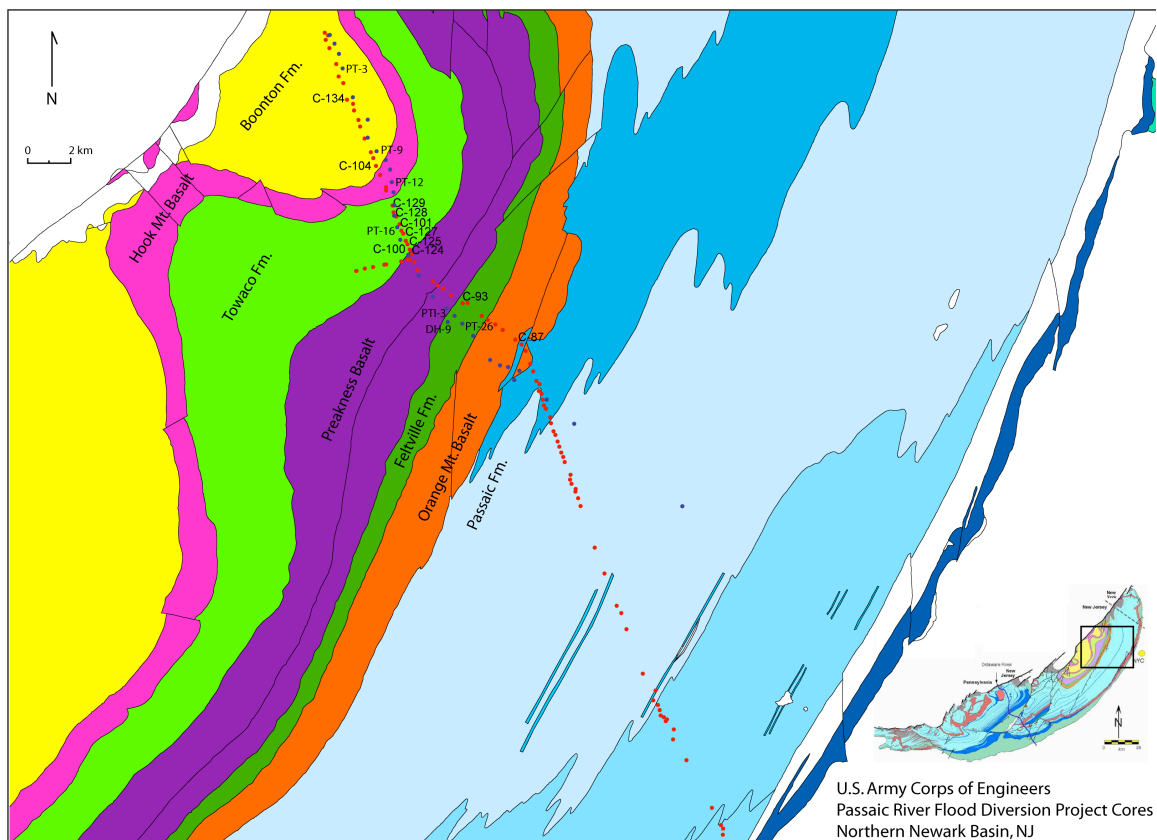


Figure 3.S1: Map of the ACE core coring locations in the North-Western Newark Basin. Those cores with labels were used by this study.

Table 3.S1: Data table providing ACE core and sample location latitude and longitude, sampling intervals, and details of the chronostratigraphic conversion. Also in Table S1 are all the original organic isotopic values, down-profile δ_{CC} isotopic measurements with indication of those used to compute the mean, and the resulting $p\text{CO}_2$ with error.

Sample (in strat. order top to bottom)	Core	Depth in Core (feet)	Formation	feet in section (from OMB base)	meters in section (from OMB base)	kyrs from OMB base	kyr (from OMB base)	myr (OMB base)	"Absolute" Time (Myr)	$\delta^{13}\text{C}$ CatCO3	SD (see 6)	N (used in mean)	$\delta^{13}\text{C}$ organic (rounded)	analytical error ($\pm$ 1000ppm)	$p\text{CO}_2$ (\$\pm\$ 3000)
NBP73-250	ACE PT-3	250 Boonton		4684.06	1471.15	1.13	543.08	1127.41	200.36	-5.61	0.20	2	-25.67	0.12	2490
NBP73-192	ACE C-134	192 Boonton		4168.61	1268.46	1.01	428.46	1012.17	200.48	-5.11	0.05	2	-25.03	0.25	3131
NBP73-433	ACE PT-6	433 Boonton		3137.38	1026.32	0.03	583.76	583.76	200.91	-3.63	0.05	3	-25.48	0.2	5273
NBP73-433	ACE C-104	123 Boonton		3137.38	1026.32	0.03	583.76	583.76	200.91	-3.68	0.05	3	-25.61	0.25	4941
Hook Mountain Basalt															
NPT112-239	ACE PT-12	239 Towaco		2935.00	930.12	311.98	575.68	575.68	200.91	-6.04	0.06	2	-25.17	0.25	1949
NPT112-239	ACE C-129	223 Towaco		2430.59	787.44	201.62	465.33	465.33	201.02	-6.18	0.32	2	-25.04	0.12	2386
NTC128-221	ACE C-128	221 Towaco		2248.58	737.72	151.95	415.67	415.67	201.07	-4.36	0.29	3	-25.91	0.2	3708
NTC101-128	ACE C-101	128 Towaco		2087.13	684.75	107.91	371.62	371.62	201.12	-5.78	0.05	2	-25.07	0.2	2642
NTC127-192	ACE C-127	192 Towaco		1923.33	633.33	327.04	327.04	327.04	201.16	-5.05	0.15	1	-25.34	0.2	3460
NPT116-266	ACE PT-16	266 Towaco		1788.33	586.72	26.38	290.09	290.09	201.20	-5.55	0.05	3	-25.30	0.25	3014
NTC125-110	ACE C-125	110 Towaco		1745.48	572.66	14.69	278.40	278.40	201.21	-4.53	0.12	2	-25.03	0.2	3657
NTC100-195	ACE C-100	195 Towaco		1745.48	572.66	14.69	278.40	278.40	201.21	-4.53	0.12	2	-25.03	0.25	4015
NPT116-340	ACE PT-16	340 Towaco		1730.62	567.79	10.63	274.36	274.36	201.22	-4.01	0.07	2	-25.88	0.2	4050
NTC124-73	ACE C-124	73 Towaco		1685.61	566.31	0.00	263.71	263.71	201.23	-4.09	0.10	2	-25.62	0.12	4070
NTC125-170	ACE C-125	170 Towaco		1685.59	566.30	0.00	263.71	263.71	201.23	-4.46	0.22	3	-25.53	0.2	4234
Peakness Basalt															
NFT113-156	ACE PTI-3	156 Feltville		865.00	260.35	233.44	233.44	233.44	201.26	-4.85	0.08	3	-25.14	0.2	3453
NFDH9-105	ACE DH-9	105 Feltville		851.31	279.30	212.45	212.45	212.45	201.28	-4.16	0.07	2	-25.55	0.12	3577
NFC33-134	ACE C-63	134 Feltville		674.23	221.21	102.15	102.15	102.15	201.39	-4.64	0.05	3	-25.06	0.2	3584
NFT28-169	ACE PT-20	169 Feltville		568.27	186.44	36.15	36.15	36.15	201.45	-3.72	0.05	2	-25.74	0.25	4228
NFT28-245	ACE PT-20	245 Feltville		514.46	168.79	0.00	0.00	0.00	201.49	-4.56	0.35	3	-25.81	0.2	4434
Orange Mountain Basalt															
NPEX	Outcrop	Passaic - Exeter I		-44.59	-13.59	-19.10	-19.10	-19.10	201.51	-3.58	0.42	3	-25.67	0.25	1065
NPMart-1342	NBCP Martinsville	1342 Passaic		-135.19	-44.35	-236.14	-236.14	-236.14	201.73	-5.91	0.05	3	-25.75	0.12	1787
NPMart-1400-1406	NBCP Martinsville	1400 Passaic		-185.27	-60.78	-323.02	-323.02	-323.02	201.81	-5.2	0.23	3	-25.60	0.12	2242
NFC87-377	ACE C-87	377 Passaic		-221.40	-72.04	-386.75	-386.75	-386.75	201.88	-4.90	0.05	3	-25.59	0.25	2253
NPMart-1643.6	NBCP Martinsville	1643.6 Passaic		-333.14	-108.49	-632.97	-632.97	-632.97	202.07	-5.79	0.05	1	-25.15	0.12	2259
NPMart-1643.6	NBCP Martinsville	1643.6 Passaic		-333.14	-108.49	-632.97	-632.97	-632.97	202.07	-5.79	0.05	1	-25.15	0.12	2259
NPMart-2055	NBCP Martinsville	2055 Passaic		-584.09	-181.83	-1030.29	-1030.29	-1030.29	202.51	-6.11	0.35	2	-25.08	0.12	2416
NPMart-2462	NBCP Martinsville	2462 Passaic		-593.20	-275.00	-1454.17	-1454.17	-1454.17	202.58	-5.41	0.05	2	-25.08	0.12	2231
NPMart-2583	NBCP Martinsville	2583 Passaic		-611.80	-301.17	-1603.49	-1603.49	-1603.49	203.69	-5.67	0.4	2	-25.02	0.12	1537
Npoo	Outcrop	Passaic - OO Mb		-191.80	-381.01	-202.83	-202.83	-202.83	203.69	-5.67	0.4	2	-25.02	0.12	1537
NPMart-3143-3156	NBCP Martinsville	3143 Passaic		-1272.23	-417.40	-2223.32	-2223.32	-2223.32	203.71	-5.47	0.05	2	-25.94	0.12	2752
NPMart-3380	NBCP Martinsville	3380 Passaic		-1405.77	-461.21	-2455.00	-2455.00	-2455.00	203.85	-7.84	0.24	2	-25.03	0.12	1475

Data/conversion source:

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 - SD is the calculated standard deviation around the down-profile means. Where n=3, the range is used. Where either range or SD < 10 analytical error, σ of 0.05 is used. A 1 permille range in δ_{CC} results in ± 100 ppm $p\text{CO}_2$, well enveloped by the error.
 - All original down-profile values: δ_{CC} isotopic values are shown in the tabs below, organized by formation. Those values used in computing the mean are highlighted.

All cores are available at the Rutgers University Core Repository

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Detailed methodology and all original analytical data are available as supporting material on *Science Online*.

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Chapter 3S: Supplement to Chapter 3

Reply to “Atmospheric pCO₂ Perturbations Associated with the Central Atlantic Magmatic Province – Technical Comment” by M. R. Rampino and K. Caldeira²

3S.1. Abstract

Caldeira and Rampino (2011) argue that the first pulse of the Central Atlantic Magmatic Province (CAMP) would increase the concentration of atmospheric carbon dioxide (pCO₂) by only 400 parts per million, if erupted over 20,000 years, whereas we (Schaller et al., 2011) observe a doubling within this interval. In the absence of any data to the contrary, we suggest that a more rapid (≤ 1000 -year) eruption is sufficient to explain this observation without relying on thermogenic degassing.

3S.2. Effusive flux estimate and observations from the Newark

Our observations from the Newark Basin indicate that the first pulse of the Triassic-Jurassic Central Atlantic Magmatic Province (CAMP), represented by the Orange Mountain Basalt, was emplaced within a precession cycle and resulted in a doubling of the atmospheric partial pressure of CO₂ (pCO₂) above pre-eruptive background. A simple model with instantaneous degassing (<1000 years (ky), within the timescale of ocean overturning) of 2.5×10^{17} moles of CO₂ ($\sim 1.2 \times 10^{16}$ kg), roughly the efflux potential of the first volcanic pulse, gives a ~ 1400 parts per million (ppm) increase

² Schaller, M.F., Wright, J.D., Kent, D.V., 2011, Response to Comment on "Atmospheric pCO₂ Perturbations Associated with the Central Atlantic Magmatic Province": Science, v. 334, no. 6056, p. 594.

in pCO₂ above the ~2000 ppm background level (Schaller et al., 2011). This estimate is compatible with, and (admittedly, barely) within the error of the doubling from ~2000 to 4400 ± 1200 ppm observed in the Newark basin. Rampino and Caldeira (2011) present a model whereby a 20 kyr release of the same magnitude produces only a ~400 ppm atmospheric pCO₂ increase, which they take as an indication that an additional source of CO₂ is necessary to explain the observed pCO₂ increase. We do not dispute this point, but it begs qualification.

3S.3. A paradox of release size

The cycle stratigraphic record from the Newark basin provides a constraint on the maximum duration (<20 kyr) of the first pulse of magmatism, but we are not aware of any data (e.g., weathering at the tops of individual lava flows or accumulation of sediments between flows) that precludes a much more rapid release. Therefore, these release-time constraints provide two useful end-member scenarios to explain the observed changes in pCO₂: Either the CO₂ release was rapid and could be almost exclusively volcanogenic, or it was more protracted, which would require nearly 10-times as much CO₂ (e.g., see Beerling and Berner, 2002; Berner and Beerling, 2007) (10^{17} moles atmospheric reservoir versus 10^{18} moles atmosphere-ocean reservoir (Berner and Caldeira, 1997; Berner et al., 1983; Caldeira and Rau, 2000; Trenberth, 1981)), opening the possibility that it may be thermogenic in origin.

Because thermogenic evolution of CO₂ from CaCO₃ sediments is an unlikely source (e.g., Kerrick and Connolly, 2001), the next largest reactive carbon pool in Earth's crust is organic, which implies that the extra CO₂ needed for a protracted release would be relatively depleted in ¹³C. However, the organic carbon δ¹³C measurements from the

Newark basin (Schaller et al., 2011) do not indicate a substantially larger ^{13}C -depleted component in the overall atmospheric pCO_2 increase, although there is a slight $\delta^{13}\text{C}$ decrease ($\sim 0.5\text{‰}$) above each volcanic unit. We note that some marine sections record a potential light carbon-isotope excursion at about this time (Hesselbo et al., 2002); however, the exact relationship of the marine $\delta^{13}\text{C}$ decrease to the CAMP eruptions remains unclear (e.g., see Whiteside et al., 2010). Moreover, our observation of comparable pCO_2 and $\delta^{13}\text{C}$ changes following the second and third volcanic events would require a similar thermogenic input if the duration of each pulse was ~ 20 kyr, which would represent a substantial repeated flux of thermogenic CO_2 to the atmosphere at discrete intervals.

Therefore, we are left to speculate on the precise source of the CO_2 pulse recorded in the Newark basin, which is essentially an argument of release duration versus size. In the absence of any data to the contrary, we favor a rapid release that allows the majority of each perturbation to be volcanogenic, but that does not preclude a metamorphic carbon source. The doubling of pCO_2 observed after each volcanic unit in the Newark basin is broadly consistent with other lower resolution studies that indicate a tripling to quadrupling through the interval (Beerling, 2002; McElwain et al., 1999; Steinthorsdottir et al., 2011). The continued challenge to the modeling community is to devise a scenario that conforms to these observations.

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Chapter 4

Rapid emplacement of the Central Atlantic Magmatic Province as a net sink for CO₂³

4.1. Abstract

Recent evidence from the ~201.5 Ma Central Atlantic Magmatic Province (CAMP) in the Newark rift basin demonstrates that this Large Igneous Province produced a transient doubling of atmospheric pCO₂, followed by a falloff to pre-eruptive concentrations over ~300 kyr. This paper confirms the short-term findings from the Newark basin, and tests the million-year effects of the CAMP volcanism on Early Jurassic pCO₂ from strata in the corollary Hartford basin of Eastern North America (ENA) also using the pedogenic carbonate paleobarometer. We find pCO₂ levels for pre-CAMP background of 2000 ± 700 ppm (at S(z) = 3000 ± 1000 ppm), increasing to ~5000 ± 1700 ppm immediately above the first lava flow unit, consistent with observations from the Newark. The longer post-extrusive Portland Formation of the Hartford basin records a fourth pulse of pCO₂ to ~4500 ± 1200 ppm, about 240 kyr after the last lava recorded in the ENA section. We interpret this fourth increase as due to a major episode of volcanism, and revise the main CAMP duration to 840 ± 60 kyr. The Portland also records a post-eruptive decrease in pCO₂ reaching pre-eruptive background concentrations of ~2000 ppm in only ~300 kyr, and continuing to levels below pre-CAMP background over the subsequent 1.5 Myr following the final episode of eruptions. Geochemical modeling (using modified COPSE

³ Schaller, M. F., Wright, J. D., Kent, D. V., and Olsen, P. E., 2011, Rapid emplacement of the Central Atlantic Magmatic Province as a net sink for CO₂: Earth and Planetary Science Letters, In Review.

code) demonstrates that the rapidity of the $p\text{CO}_2$ decreases, and fall to concentrations below background can be accounted for by a 1.5-fold amplification of the continental silicate weathering response due to the presence of the CAMP basalts themselves. These results demonstrate that a continental flood basalt capable of producing a short-term perturbation of the carbon system may actually have an overall net-cooling effect on global climates due to a long-term net-decrease in $p\text{CO}_2$ to below pre-eruptive levels, as previous models have suggested followed emplacement of the Deccan Traps.

Keywords: Large Igneous Province, Atmospheric Carbon Dioxide, Triassic-Jurassic, CO_2 Chemical Weathering

4.2. Introduction

Covering millions of square kilometers of continental area, continental flood basalts are Large Igneous Provinces (LIPs) that may produce in excess of several million cubic kilometers of lava (Coffin and Eldholm, 1993). The great volume and aerial extent of these eruptions, and their intriguing association with mass extinction events throughout earth history (Courtilot and Renne, 2003; Wignall, 2001), has spurred interest in the potential of LIPs to alter the composition of Earth's atmosphere through the emission of gases – primarily SO_2 and CO_2 (Self et al., 2008). Until recently, geochemical modeling and effusive flux estimates seemed to suggest that CO_2 degassed during continental flood volcanism probably has a negligible long-term effect on the atmosphere (e.g., Caldeira and Rampino, 1990; Self et al., 2006). Most recently, Schaller et al. (2011a) tested the direct effects of a LIP using the pedogenic carbonate paleobarometer (Cerling, 1999) on sediments in superposition with the extrusives of the Triassic-Jurassic Central Atlantic

Magmatic Province (CAMP) in the Newark basin of eastern North America (Fig. 4.1).

Schaller et al. (2011a) demonstrated that the short term ($10^4 - 10^5$ -year) effects of a continental flood basalt on atmospheric $p\text{CO}_2$ may be substantial – a doubling of $p\text{CO}_2$ in apparent response to each magmatic episode – and yet quite transient with a steady decrease in atmospheric $p\text{CO}_2$ over the ~ 300 kyr following each volcanic episode.

Several independent geochemical models have predicted such a transient response following the eruption of the Deccan Traps (Caldeira and Rampino, 1990; Dessert et al., 2001). The model of Dessert et al. (2001) specifically predicts atmospheric CO_2 concentrations falling some 20% below pre-eruptive background by about 1 million years after the eruption of the Deccan Traps, an effect attributed to an acceleration of global silicate weathering further amplified by the presence of fresh weatherable basalt. However, due to the absence of continuous sedimentary sections where the appropriate lithology interbedded with volcanics, such a response to any LIP other than the CAMP has not yet been explicitly identified. Encouragingly, immediately post-eruptive $p\text{CO}_2$ decreases have been observed in the Newark basin following the CAMP eruptions (Schaller et al., 2011a), and the corollary Hartford basin of eastern North America contains a much longer post-extrusive section (Kent and Olsen, 2008) where the long-term response of the system may be tested. In this paper we first use the pedogenic carbonate paleobarometer (Cerling, 1999) to demonstrate increases in $p\text{CO}_2$ coincident with pulses of CAMP volcanism in the equivalent strata of the Hartford basin. We further use the thick post-CAMP Portland Formation to evaluate the long-term decrease in $p\text{CO}_2$ as a function of increased global silicate weathering, testing the hypothesis that

the presence of $2 - 4 \times 10^6 \text{ km}^3$ of fresh CAMP basalt (McHone, 2003) is capable of reducing $p\text{CO}_2$ to below pre-eruptive background concentrations.

4.3. The CAMP record in the Newark and Hartford basins

The Central Atlantic Magmatic Province (CAMP; Marzoli et al., 1999) is perhaps the largest continental flood basalt of the Phanerozoic, with latest Triassic and earliest Jurassic tholeiitic basalts and mafic intrusions preserved on four continents, and an aerial extent of greater than $1.12 \times 10^7 \text{ km}^2$ (McHone, 2003) (Fig. 4.1). CAMP basalts span the Mesozoic rift zone of the Pangean supercontinent, and despite heavy erosion, are well exposed in the rift basins of eastern North America and Morocco, where they have been extensively studied. More poorly understood constituents of the CAMP are preserved in West Africa, Europe, and extensive regions of South America. However, $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric ages for this vast collection of lava flows and intrusives are essentially indistinguishable within the dating error (e.g., Hames et al., 2000; Jourdan et al., 2009; Knight et al., 2004; Marzoli et al., 2004; Marzoli et al., 2011; Nomade et al., 2007; Verati et al., 2007), and center the eruptive events around $\sim 201 \text{ Ma}$. More precise U-Pb dates place some of the first flow units at $201.38 \pm 0.31 \text{ Ma}$ (Schoene et al., 2010) in Eastern North America.

The half-graben rift basins of the Newark Supergroup in Eastern North America contain Late Triassic to Early Jurassic age strata, the majority of which are shallow to deep lacustrine, fluvial, alluvial and playa facies (Olsen, 1997; Smoot, 1991). The lacustrine sedimentary units in each basin display a rhythmic succession of facies that reflect periodic fluctuations in lake depth (Van Houten, 1962), which have been related

directly to Milankovitch orbital forcing of tropical precipitation (Olsen, 1986; Olsen and Kent, 1996). The stratigraphy of the Newark basin is precisely known from a continuous cored section through the center of the basin (Kent et al., 1995; Olsen et al., 1996a), and this record of orbitally forced sedimentation provides the astronomical chronometer used to construct the geomagnetic polarity time scale for more than 32 Myr of the Late Triassic and Early Jurassic (Kent and Olsen, 1999; Kent et al., 1995; Olsen and Kent, 1996, 1999).

The CAMP extrusive interval sits at the top of the Newark basin section and is composed of three lava flow units (stratigraphically upward, the Orange Mountain, Preakness, and Hook Mountain Basalts), with significant sedimentary sequences above each of them (Feltville, Towaco, and Boonton Formations, respectively) (Figs. 1 and 4). Milankovitch cycle-stratigraphy on these sediments has constrained the duration of volcanism in the Newark basin to $\sim 600 \pm 20$ kyr (Olsen et al., 2003; Olsen et al., 1996b; Whiteside et al., 2007), where the Feltville Formation represents ~ 260 kyr, the Towaco Formation ~ 290 kyr; the first flow unit (Orange Mountain Basalt) was apparently extruded within a single precession cycle. The Hook Mountain Basalt is also within a precession cycle whereas the duration of the Preakness Basalt can presently only be constrained to $\sim 60 \pm 20$ kyr (Whiteside et al., 2007). In these primarily lacustrine units, paleosols with varying degrees of pedogenic carbonate development had formed during the dry phases associated with low lake depth. Schaller et al. (2011a) used these soils to test both the magnitude and duration of the effects of the CAMP volcanism on atmospheric $p\text{CO}_2$.

In the Hartford basin, the oldest strata are the fluvial and marginal lacustrine facies of the Triassic New Haven Formation, where pedogenic carbonate-bearing paleosols are abundant (Hubert, 1978). The first volcanic unit is the Talcott Basalt, followed by the Holyoke and Hampden basalts, interbedded with the cyclic lacustrine sequences of the Shuttle Meadow and East Berlin Formations and the Smith's Ferry and Park River members of the lower Portland Formation) (Figs. 1 and 3). Interspersed throughout these lake sequences are more weakly developed paleosols, where periodic subaerial exposure of the primary sediments allowed soil-forming processes to operate on the lake margins (e.g., Tanner, 2003).

The predictive framework of Milankovitch cycle stratigraphy has been used to demonstrate that the flow units and interbedded sedimentary sequences of the Hartford basin are directly equivalent to those present in the Newark basin (Olsen, 1988; Whiteside et al., 2007) (Figs. 1 and 4). Therefore, the Shuttle Meadow Formation represents ~260 kyr, and the East Berlin Formation ~290 kyr. Recently, the magnetostratigraphy of the Hartford basin has extended the Newark timescale into the Early Jurassic (Kent and Olsen, 2008), through sampling of the largely lacustrine lower 2000 meters of the thick post-extrusive Portland Formation, which is the primary focus of the current study.

4.4. Estimating $p\text{CO}_2$ from pedogenic carbonates

Pedogenic carbonate nodules were collected from paleosols located stratigraphically above and below each of the CAMP flows in the Hartford basin from both cores and outcrop. Samples from New Haven Formation, distributed 500 and 1200

meters below the Talcott Basalt, provided a pre-CAMP baseline. Since the mostly fluvial New Haven lacks cycle or magnetic stratigraphy, these samples are treated as a single relative background value for comparison to the Newark basin record. The samples situated ~1200 m below the Talcott Basalt are from exposures dated using U-Pb at 211 ± 2.1 Ma by Wang et al. (1998), and we estimate the sample at 500m below the basalt to be ~205 Ma. Samples from the lower Shuttle Meadow Formation are from a cored section near Berlin, CT (Silver Ridge Core B-1 (see Whiteside et al., 2011)) as well as from outcrop. The upper 75% of the East Berlin Formation is well exposed but suitable paleosols are rare. The lower 600 m of the post-extrusive Portland Formation is covered in high resolution with significant overlap by a series of short geotechnical cores taken by the Army Corps of Engineers (ACE) during construction of the Park River flood diversion tunnel project (Kent and Olsen, 2008; Pienkowski and Steinen, 1995). Samples from exposures in the middle to upper Portland Formation were assembled using the stratigraphy of Kent and Olsen (2008), and our upper-most sample is from near the top of the mostly lacustrine part of the Portland Formation (see Table 1 for all sample and core location data).

Organic and inorganic carbon isotope measurements from these paleosols were input into the soil diffusion model of Cerling (1999):

$$C_a = S(z) \frac{\delta_s - 1.0044\delta_\phi - 4.4}{\delta_a - \delta_s}$$

where C_a is the concentration of atmospheric CO_2 , $S(z)$ is the concentration of CO_2 at soil depths greater than 50cm contributed by the respiration of soil organic matter, δ_s is the $\delta^{13}\text{C}$ of soil CO_2 , δ_ϕ is the $\delta^{13}\text{C}$ of soil-respired CO_2 , and δ_a is the $\delta^{13}\text{C}$ of atmospheric CO_2 . All δ values are relative to Vienna PeeDee Belemnite (VPDB).

The carbon isotopic ratio of soil carbonate (δ_{cc}) is used as a proxy for δ_s , which involves a temperature-dependent equilibrium fractionation between CaCO_3 and CO_2 , described by:

$$10^3 \ln \alpha = 11.709 - 0.116(T) + 2.16 \times 10^{-4} (T)^2 \quad (\text{Cerling, 1999})$$

where α is the fractionation factor, and temperature (T , in $^\circ\text{C}$) is fixed at 25°C , as appropriate for the tropical Newark basin. Because there is no carbon isotope fractionation due to respiration, δ_ϕ is related directly to the carbon isotopic ratio of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$). The carbon isotopic ratio of the atmosphere is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by the following relationship (Arens et al., 2000):

$$\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10$$

which assumes consistent fractionation by photosynthesis. This builds carbon cycle perturbations directly into the model. The only adjustable parameter of the model is the concentration of CO_2 in the soil derived from the respiration of organic matter ($S(z)$), which is a function of soil productivity. The paleosols sampled in this study were relatively productive argillic and vertic calcisols (Mack et al., 1993), with mean depth to the Bk horizon (D_s) at 40 ± 15 cm soil depth, which we use to estimate $S(z)$ by the following empirical relationship: $S(z) = 66.7D_s + 588$ (Retallack, 2009). This results in a mean $S(z)$ of ~ 3256 with an SE of ± 893 ppm. Given the difficulty inherent in accurately estimating depth to the Bk horizon in individual paleosols from drill cores, and in accordance with the work of Breecker et al. (2009, 2010), we use an $S(z)$ value of 3000 ± 1000 ppm for all pCO_2 estimates, which gives a final pCO_2 range that is indistinguishable from the error that would result from systematic use of the empirical depth to carbonate

relationship. Individual soil profiles were not decompacted (Retallack, 2009), and our $S(z)$ approximations are therefore conservatively low.

A combination of thin sections and polished slabs are used to identify primary micritic calcite from diagenetic material (Driese and Mora, 2002), with a sampling preference for small, isolated carbonate nodules that are generally in better isotopic equilibrium with the surrounding soil than larger nodules or calcretes (Schaller et al., 2011a). Great care was taken to avoid phreatic calcretes, and to sample only those displaying clear evidence of having formed in the vadose zone (Rasbury et al., 2006). Samples for organic carbon isotope analysis were taken from as close to the soil-surface as possible to avoid measuring recalcitrant organics unrelated to the active organic carbon pool during soil formation (Nadelhoffer and Fry, 1988), and several samples from each profile were homogenized to provide a more representative organic carbon value.

The $\delta^{13}\text{C}$ value of pedogenic carbonate is known to decrease predictably with soil depth (Quade et al., 1989), and characterizing this trend makes it possible to differentiate between the relative influences of the atmospheric vs. soil-respired CO_2 reservoirs. Therefore, multiple (at least 5) down profile isotopic measurements were made on each paleosol to identify an equilibrium δ_{cc} value with depth in the soil (Schaller et al., 2011a) (Fig. 4.2). Using the mean of these depth-controlled measurements ensures that the mixing between the atmospheric and soil-respired reservoirs is at equilibrium with respect to the diffusion model, removing significant uncertainty in the isotopic maturity of a given paleosol profile.

Chronostratigraphic placement follows the cycle and magnetic stratigraphy of Olsen et al. (2005) and Kent and Olsen (2008). In the Park River ACE core suite, this

cyclostratigraphy provides direct stratigraphic age control to the level of orbital precession, and correlates unambiguously to the post-extrusive Boonton Formation of the Newark basin (Kent and Olsen, 2008; Olsen et al., 2005).

4.5. Results

The depth-equilibrated mean stable carbon isotopic composition of pedogenic carbonate ($\delta^{13}\text{C}_{\text{cc}}$) from exposures 500 to 1200 m below the Talcott basalt in the New Haven Formation ranges from -7.7 to -7.2 ‰ (relative to VPDB), which are comparable to values from the Passaic Formation of the Newark basin (see Table 1). These values are very close to those of Suchecky et al. (1988) from the New Haven Formation, which help to establish a consistent average pre-eruptive background. Stratigraphically above the Talcott Basalt, in the lower Shuttle Meadow Formation, pedogenic carbonates have $\delta^{13}\text{C}$ values of -3.2 ‰, which decrease to -6.6 ‰ toward the top of the formation (Fig. 4.3). Comparable values of -6.3 ‰ are found at the top of the East Berlin Formation, which sits stratigraphically above the Holyoke Basalt (the second flow unit). The $\delta^{13}\text{C}$ of soil organic matter was between -26.3 and -26.0 ‰ in the Shuttle Meadow and upper East Berlin formations. These values are consistent with results from the Feltville and Towaco formations of the Newark basin (Schaller et al., 2011a), and the high $\delta^{13}\text{C}$ of pedogenic carbonate above the Talcott Basalt (equivalent of the Newark Orange Mountain Basalt) probably represents the increased influence of the atmospheric CO_2 reservoir on pedogenic carbonate formed at depth.

Calculated pCO_2 levels through the New Haven Formation are treated as a single value, averaging 1900 ± 650 ppm. Those samples from exposures roughly 1200 m below

the Talcott basalt have a U-Pb age of 211.9 ± 2.1 Ma (Table 1) (Wang et al., 1998), and calculated $p\text{CO}_2$ values of ~ 1800 to 2200 ± 700 ppm (Table 1; all $p\text{CO}_2$ estimates at $S(z) = 3000 \pm 1000$ ppm), which are comparable to the $\sim 2000 \pm 700$ ppm of Schaller et al. (2011a) from the pre-CAMP Passaic Formation (204 to 201.5 Ma) in the Newark basin. These samples from the lower New Haven indicate that a pre-eruptive Triassic $p\text{CO}_2$ baseline may have persisted for at least ~ 10 Myr before the initial CAMP eruptions, a significant extension of the available Newark record.

Just above the Talcott Basalt in the Shuttle Meadow Formation, $p\text{CO}_2$ increases to $\sim 5000 \pm 1500$ ppm followed by a decrease to $\sim 3000 \pm 1000$ ppm just beneath the Holyoke Basalt. These $p\text{CO}_2$ levels are comparable to those observed in the first post-eruptive strata of the Feltville Formation in the Newark basin, at $\sim 4400 \pm 1400$ ppm directly on top of the Orange Mountain Basalt (Fig. 4.4). Atmospheric $p\text{CO}_2$ at the top of the East Berlin Formation, just below the Hampden Basalt, is roughly 2200 ± 750 ppm, which is consistent with the ~ 2000 ppm background values found at the top of the Towaco Formation of the Newark basin (Fig. 4.4). Although the resolution of these few inter-CAMP points in the Hartford basin is sporadic, their consistency with the record from the Newark strata (Fig. 4.4) reinforces the independence of individual values and the global applicability of this approach.

In the post-extrusive Portland Formation, pedogenic carbonates have $\delta^{13}\text{C}$ values of -3 to -5 ‰ just above the Hampden Basalt, decreasing to -7 ‰ about 200 m up section (Fig. 4.3). Around 240 m above the Hampden Basalt, the $\delta^{13}\text{C}_{\text{cc}}$ again increases to -3.5 ‰, followed by a falloff through the rest of the sampled Portland Formation to a minimum of -9.5 ‰ ~ 2400 m (1.8 Myr) above the Hampden Basalt. The $\delta^{13}\text{C}$ of soil

organic matter ($\delta^{13}\text{C}_{\text{OM}}$) also shows variability through the Portland Formation, ranging from -24.9 ‰ to -27.8 ‰ (Fig. 4.3). Similar to the Newark record, $\delta^{13}\text{C}_{\text{OM}}$ decreases slightly just above the Hampden Basalt, followed by an immediate swing toward higher values. Overall, the lower Portland formation Formation exhibits ~3‰ variability in $\delta^{13}\text{C}_{\text{OM}}$ that stabilizes up section.

Calculated atmospheric pCO_2 in the Portland Formation shows a few distinct trends. In soils formed directly on top of the Hampden Basalt, pCO_2 levels are $\sim 5400 \pm 1500$ ppm, with some fluctuation in the calculated pCO_2 level before settling to $\sim 4300 \pm 1200$ ppm (Fig. 4.3). This apparent fluctuation, observed in a single core above the Hampden Basalt, is driven by the $\delta^{13}\text{C}$ of soil organic matter, because the $\delta^{13}\text{C}$ of pedogenic carbonate is relatively stable in the first 10 m above the basalt. Because these soils are relatively weakly developed and organic matter was rare, the few apparently lower pCO_2 values are likely a product of ^{13}C enriched recalcitrant organic matter that is unrelated to the active decomposition pool during pedogenesis (Nadelhoffer and Fry, 1988). Aside from these few points, the majority of the calculated pCO_2 changes in the Hartford basin appear to be driven by the $\delta^{13}\text{C}$ of pedogenic carbonate.

Above the initial increase, atmospheric pCO_2 gradually decreases to near background levels in the first 200m of the post-extrusive Portland Formation. At about 240 m above the Hampden Basalt, pCO_2 again peaks to $\sim 4500 \pm 1200$ ppm, which is captured laterally across 2 individual cores, followed by a steady decrease to below background levels through the rest of the 1700 m of sampled section (Fig. 4.3).

Because the Park River Member is equivalent to part of the Boonton Formation of the Newark basin, the pCO_2 values found in the Portland are expected to be consistent

with the Boonton record, where an increase to ~5000 ppm is noted just above the Hook Mountain Basalt (Fig. 4.4), and where the next few samples some 350 m up section yield pCO₂ levels of ~3000-2500 ppm. These values from the upper Boonton Formation were previously thought to be anomalously high, but are in fact directly consistent with similar high concentrations following the pCO₂ peak at 240 m in the Portland Formation. It appears that the full expression of the final observed pCO₂ pulse of the Portland (the fourth of the Newark-Hartford section) was simply not captured by the low resolution record from the Boonton Formation due to lack of appropriate lithology, and yet the few points present in the upper Newark match their chronostratigraphic equivalents in the Hartford. The pCO₂ estimates from the Portland Formation shows excellent reproducibility across section between overlapping individual cores. Overall, the Hartford basin pCO₂ record is tightly consistent with that of the Newark basin (~250 km to the south), despite independent age control used for correlation (error within a few precession cycles between basins) and our use of parameterized S(z) values of 3000 ± 1000 ppm, and temperatures fixed at 25°C in the records generated from both basins (Figs. 4 and 6).

4.6. A fourth major pulse of volcanism?

With one exception, each pulse of CO₂ observed in the Newark and Hartford records is found only directly above a unit of CAMP lavas, and each observed pCO₂ increase has accordingly been attributed to the volcanic activity responsible for the emplacement of the underlying extrusive unit (Schaller et al., 2011a). The observed increase in pCO₂ ~240 m from the base of the Portland Formation, or ~240 kyr after the

extrusion of the Hampden Basalt, is of roughly the same size and duration as those in the Newark and Hartford record that are directly preceded by laterally extensive extrusive units (Fig. 4.5). Also, the $\delta^{13}\text{C}$ of organic matter shows little indication of another (perhaps lighter) source of carbon feeding this CO_2 pulse (e.g., Svensen et al., 2004). Therefore we attribute this fourth rise to a fourth episode of substantial and rapid volcanism, similar in magnitude to those episodes corresponding to the observed lava flow units in the Newark and Hartford basins.

However, there is no solid evidence in Eastern North America for a fourth major pulse of CAMP activity (see Olsen et al., 2011; Weems and Olsen, 1997 for review). A thin unnamed basalt caps the Culpeper basin sequence about ~1300 m above the Sanders Basalt. However, there is structural ambiguity (Lee and Froelich, 1989), and the unnamed basalt may in fact be a faulted portion of the underlying Sanders Basalt (Weems and Olsen, 1997), making it an unlikely candidate for the volcanic episode that produced the fourth pCO_2 increase observed in the Hartford basin.

Similarly, four distinct flow units have been recognized in the corollary High Atlas region of Morocco, deemed the Lower, Intermediate and Upper Units, and the Recurrent Basalt, on the basis of major element geochemistry (Bertrand, 1991). Although there is debate regarding the detailed stratigraphic placement of the Lower Basalt (Deenen et al., 2010; Marzoli et al., 2004; Whiteside et al., 2007), the Recurrent is geochemically similar to Hook Mountain and Hampden Basalts (Deenen et al., 2010; Marzoli et al., 2011), leaving the volcanism responsible for the Recurrent a possible, but still unlikely tracer for the fourth pCO_2 increase observed in the Hartford basin. The South American CAMP extrusive section remains largely unstudied stratigraphically, and

it is unclear how these volcanics are related to the ENA section. Despite CAMP dikes, sills and rarer lava flows preserved over several million square kilometers of northern South America (see Marzoli et al., 1999 for review), it is at present impossible to determine the precise temporal or stratigraphic relationship of these volcanic units at the level necessary to isolate a single widespread eruptive event as the cause for the fourth pCO₂ pulse observed in the Hartford basin. In addition, the age(s) of the Clubhouse Crossroads Basalt and their possible relationship to the voluminous seaward-dipping reflectors offshore is unclear (Olsen et al., 2003), and hence some of this igneous activity cannot be readily dismissed as a potential source for the fourth pCO₂ pulse.

Most importantly, as evidenced by the fourth pCO₂ peak in the Hartford basin, the CAMP-induced pCO₂ increases should be identifiable in any section with the appropriate lithology and high sedimentation rate, regardless of the presence of CAMP lavas. Identifying these four pCO₂ pulses in other basins is an essential step toward understanding the stratigraphy of the extrusive zone, and potentially adds a higher degree of precision to global correlation. In that light, the identification of a fourth apparent volcanogenic pulse in the Hartford basin allows us to revise the total duration of CAMP induced high pCO₂ as observed in the ENA basins from 600 ± 20 kyr (Olsen et al., 2003; Whiteside et al., 2007), to 840 ± 60 kyr, based on the amount of time present between the base of the Talcott Basalt and the last apparent pulse of CO₂ in the Portland Formation using the chronostratigraphy of Kent and Olsen (2008).

4.7. Weathering of the CAMP basalts

A notable characteristic of the post-eruptive CAMP record is the striking decrease in atmospheric pCO₂ within a few hundred thousands years of basalt emplacement (Fig.

4.6). In the Newark record $p\text{CO}_2$ falls from an excess of ~ 4000 ppm to nearly background levels of ~ 2000 ppm within ~ 300 kyr of the extrusives. Similarly, in the post-extrusive Portland Formation of the Hartford basin, we observe a decrease over a comparable timescale (following both the Hampden Basalt and the fourth $p\text{CO}_2$ increases discussed above). Unlike the others, $p\text{CO}_2$ continues to decline following the final pulse in the Portland Formation, and ultimately levels off at concentrations below pre-eruptive background. We hypothesize that both the rapidity of the $p\text{CO}_2$ decreases, and the fall in $p\text{CO}_2$ to below background are due to the rapid consumption of CO_2 by an overall increase in continental weathering, which is accelerated by the relatively rapid hydrolysis of the freshly erupted CAMP silicates themselves.

4.7.1. Modeling the post-extrusive $p\text{CO}_2$ decrease

Here, we use a geochemical model to demonstrate that the rapid decrease in atmospheric $p\text{CO}_2$ following the CAMP eruptions may indeed be due to basalt-induced amplification of the predicted increase in continental weathering. We use a modified version of the COPSE biogeochemical model (Bergman et al., 2004) in perturbation mode, which couples the carbon, oxygen, phosphorus and sulfur cycles, with explicit feedbacks between atmospheric $p\text{CO}_2$ and temperature to the rate of continental silicate weathering.

In the case of the Orange Mountain Basalt in the Newark basin (the oldest flow unit), the duration of eruption is well constrained to within a single precession cycle (Olsen et al., 2003; Whiteside et al., 2007), and a doubling of $p\text{CO}_2$ over pre-eruptive background is observed directly on top of the uppermost lava flow of the Orange

Mountain. Each volcanic episode shows roughly the same $p\text{CO}_2$ response, with a similar durational constraint (with the exception of the Preakness and equivalent Holyoke basalts), and we are not aware of any data, geochemical or otherwise, that precludes an eruption time as short as 1000 years (1 kyr) for a single extrusive unit. The absence of significant sedimentary strata or deep weathering profiles between individual lava flows of a single extrusive unit (e.g., within the Hampden Basalt) favors a short amount of time between lava flows, especially considering the high long-term sediment accumulation rates of ~ 1 meter per thousand years (Kent and Olsen, 2008). Therefore, we use a total eruptive duration of 1000 years for a single extrusive unit in our geochemical modeling, and for reference, show the results of a 10,000-year (10 kyr) degassing scenario with an identical release.

The perturbation mode of the modified COPSE model starts from a 100 kyr steady state where mid-ocean ridge degassing is balanced by silicate weathering as a function of $p\text{CO}_2$ and temperature at initial conditions. The model couples the surface ocean-atmospheric C-reservoir on a 1000-yr time-scale, and runs at 100-yr timesteps. In our simulations, we roughly double the size of the atmospheric fraction of the coupled ocean-atmosphere reservoir by adding 3.5×10^{17} moles of CO_2 over 1000 years to reproduce the observed doubling of atmospheric CO_2 immediately following the CAMP eruptions, which is roughly one third of the total CO_2 potentially degassed from a total estimated CAMP basalt volume of the $\sim 3 \times 10^6 \text{ km}^3$ (Schaller et al., 2011a, b; Self et al., 2006). We run the model for a total of 1900 kyr, and in the reference run simply watch the weathering response of the system to this doubling over the ensuing 1800 kyr of model time. In an attempt to simulate the effect of an increase in the weathering potential

of the continental surface, we further amplify the increased rate of continental silicate weathering at the time of CO₂ perturbation by 1.5- and 2-times the normal effect.

4.7.2. Model results

The reference simulation shows the prescribed doubling of pCO₂ after the 100 kyr steady state, followed by an asymptotic drawdown to relatively stable pCO₂ levels that are slightly higher than the pre-perturbation steady-state by 600 kyr after the release (Fig. 4.5, red line). This suggests that the silicate weathering system is capable of removing the majority of a doubling perturbation within ~600 kyr, but the increase in weathering due to the rapid transient increase in pCO₂ (and greenhouse temperature) is not enough to lower pCO₂ levels below pre-eruptive background, as observed in the post-CAMP record from the Hartford basin.

A 1.5-times amplification of the increased weathering rate at the time of CO₂ perturbation returns the system to pre-eruptive background pCO₂ levels by ~270 kyr, and eventually falls to about 20% below steady-state background (Fig. 4.5, blue line). A 2-times amplification returns pCO₂ to background levels by 180 kyr post-perturbation, eventually falling to well below pre-eruptive background (~30%) for the remaining 1500 kyr of simulation (Fig. 4.5, green line). The 10 kyr reference simulations (Fig. 4.5, black and gray dashed lines) both show roughly 12% of the initial atmospheric pCO₂ response as the 1 kyr runs using the same 3.5×10^{17} mole release.

The pCO₂ decreases to below pre-eruptive background in the Portland Formation cannot be a function of a normal increase in weathering due to a CO₂ perturbation (as in the reference run), indicating that some amplification of the weathering increase is

required. However, a 2-times amplification (above the background increase due to increased temperature and CO₂ alone) reduces pCO₂ to levels further below background than observed in the Portland Formation. Therefore, we suggest a ca. 1.5-times amplification of the silicate weathering increase adequately describes the two post-eruptive decreases observed in the Portland. This demonstrates that the highly weatherable basalts erupted into the equatorial humid belt must be partially responsible for the rapidity of the pCO₂ drawdown, and the decrease to below pre-eruptive background, by amplifying the increased in global weathering rates by perhaps 1.5-times. It should be noted that the timing and duration of the pCO₂ fluctuations are well-constrained parameters of the Newark-Hartford pCO₂ record, due to the precision of the astrochronology on these strata (Kent and Olsen, 1999, 2008; Olsen and Kent, 1996; Olsen et al., 1996a; Olsen et al., 2003). Therefore, the rate of drawdown is entirely dependent on calculated pCO₂ values and not an artifact of poor age control.

Since the difference between the test simulations and the reference run is essentially a function of basalt area available for hydrolysis, we can estimate the proportion of basalt necessary to further amplify the rate of continental weathering by a factor of 1.5. Assuming that a continental flood basalt may weather at a rate 10-times that of granitic continental crust (Dessert et al., 2003; Gaillardet et al., 1999), increasing the weathering potential of the total continental surface by a factor of 1.5 may be achieved by erupting enough basalt to cover $\sim 1/18^{\text{th}}$ the continental area, or $\sim 8.3 \times 10^6$ km² (assuming total land area of roughly 1.5×10^8 km²). This figure is comparable to estimates of the CAMP eruptive area at 1.12×10^7 km² (McHone, 2003). Additionally, it appears that the rate of post-extrusive drawdown is faster in the later part of the

composite Newark-Hartford record than earlier in the eruptive history (see Fig. 4.6).

This may be due to the continuously increasing amount of basalt available to participate in weathering reactions with increasing time from the initial eruptions.

4.7.3. Comparison to the Deccan

Modeling experiments similar to those performed here have been used to evaluate the effects of the Deccan LIP (Caldeira and Rampino, 1990; Dessert et al., 2001), which lacks direct estimates of $p\text{CO}_2$. In their most aggressive eruptive scenario, Caldeira and Rampino (1990) release 2.0×10^{17} moles CO_2 over an eruptive duration of 100 kyr, resulting in a meager ~ 65 ppm increase in $p\text{CO}_2$. This CO_2 release is close to that used in the present study, but Caldeira and Rampino (1990) assume a much longer eruptive duration, which results in a highly attenuated effect. They find that equilibrium is reestablished ~ 1.5 Myr after the eruption of the Deccan Traps; however, their model incorporates only a modest increase in continental weathering at the time of perturbation, and does not include an amplification to account for the Deccan basalts, so $p\text{CO}_2$ does not fall below pre-eruptive background.

In contrast, Dessert et al. (2001) use a much larger single CO_2 release (1.6×10^{18} moles CO_2 over 100 kyr), which amounts to a ~ 1800 ppm increase, or a little over a doubling of atmospheric $p\text{CO}_2$, which is similar to the increase observed in response to the CAMP. More importantly, the presence of the Deccan basalts themselves resulted in the return of $p\text{CO}_2$ to pre-eruptive levels by 1.2 Myr after perturbation, followed by a continued decline to equilibrium at levels 20% lower than pre-eruptive concentrations. They conclude that the increased continental weathering potential afforded by the

presence of the Deccan lava pile was essential in rapidly reducing atmospheric $p\text{CO}_2$ below steady state background.

The results of Dessert et al. (2001) for the Deccan are consistent with the findings of this study of the CAMP, but have a significantly longer relaxation time: $p\text{CO}_2$ does not return to pre-eruptive background until ~ 1.2 Myr after perturbation in the Dessert et al. (2001) simulation, compared to the ~ 300 kyr return observed in the CAMP record. Several factors probably account for this difference. First, the Dessert et al. (2001) simulation releases a large quantity of CO_2 over a relatively long eruptive period (100 kyr) to induce a $\sim$ doubling of atmospheric $p\text{CO}_2$, which may take a significantly longer amount of time to remove completely. A much smaller total amount of CO_2 can be released over a much shorter duration (e.g., 3.5×10^{17} released over 1000 years, as in our simulations) and result in roughly the same doubling of atmospheric $p\text{CO}_2$. Thus, on timescales greater than 1000 years, or the nominal overturning time of the oceans (Broecker and Peng, 1982), nearly 10-times more CO_2 is needed to produce the same atmospheric effect, which may require additional CO_2 sources. This is apparent in our simulations (Fig. 4.5) where 3.5×10^{17} moles of CO_2 are released on both 10 kyr and 1 kyr timescales; the 10 kyr release resulted in $\sim 12\%$ of the initial atmospheric $p\text{CO}_2$ increase as that of the 1 kyr scenario. Secondly, a more minor contributing factor is that the weatherable area of the Deccan Traps was estimated to be $\sim 2 \times 10^6 \text{ km}^2$, which is considerably smaller than the total estimated area of the CAMP eruptions ($\sim 1.12 \times 10^7 \text{ km}^2$), and hence has a more limited potential to absorb CO_2 . Thirdly, CAMP straddled the paleoequator where weathering may have been more intense than that of the Deccan, which was emplaced in the tropical arid belt ($\sim 26^\circ\text{S}$ latitude) although it was subject to

more intense weathering much later when India drifted into the equatorial humid belt (Kent and Muttoni, 2008).

Parenthetically, the rate of CO₂ release will also affect the degree of ocean acidification. Hautmann (2004) hypothesized that drastic increases in pCO₂ around the Triassic-Jurassic transition may have caused rapid ocean acidification, and hence undersaturation of seawater with respect to CaCO₃, based on a global carbonate gap in the stratigraphic record. Berner and Beerling (2007) use a geochemical model to test this hypothesis, and conclude that a minimum release of 8.3×10^{17} moles CO₂ (10,000 GtC) in less than 100 kyr is necessary to induce wide-spread CaCO₃ dissolution. However, a degassing scenario where $\sim 3 \times 10^{17}$ moles CO₂ are released in ~ 1 kyr, as we suggest is recorded in the Newark Group where four such pulses of roughly $\sim 3.5 \times 10^{17}$ moles CO₂ each are observed, is probably sufficient to produce a CaCO₃ undersaturated ocean.

6.4. Other indicators of increased pCO₂ and global weathering rates

Our pCO₂ estimates are corroborated by other independent reconstructions at lower resolutions. In particular, stomatal densities have shown a doubling to tripling of pCO₂ across the ETE, followed by a 600 kyr plateau at elevated concentrations (McElwain et al., 1999). Despite showing the same relative change as the Newark Group paleosol estimates, the absolute values of the stomata-based approximations are appreciably lower and show little variability within the CAMP interval. This apparent lack of resolution within the CAMP interval is probably because both the stomatal index and density proxies have an asymptotic response to increasing pCO₂ (Beerling and Royer, 2002b), and therefore become insensitive at extremely high concentrations,

showing little further change as saturation is approached. The offset between the paleosol estimates and the leaf stomata record may also be due to calibration issues, where the stomatal density proxy may underestimate $p\text{CO}_2$ (Beerling and Royer, 2002a).

Pedogenic carbonate $p\text{CO}_2$ reconstructions from the western U.S. (Cleveland et al., 2008) are comparable to the pre-eruptive background levels found in the New Haven and Passaic formations of this study. The Ghost Ranch and Montoya sections of Cleveland et al. (2008) lack CAMP volcanics and instead rely on a chronology derived from fluvial sequence stratigraphy (Cleveland et al., 2007). Without evidence that these sections extend into the Early Jurassic, long distance-correlation to the Newark record at the stage level overlaps the Ghost Ranch and Montoya $p\text{CO}_2$ estimates with our pre-CAMP baseline. Although their estimates are highly variable, they are not inconsistent with pre-CAMP data from the Passaic (Schaller et al., 2011a) or New Haven Formations presented here ($\sim 2000 \pm 700$ ppm). The variability in the Cleveland et al. (2008) data can be attributed to their lack of multiple down-profile isotope measurements, such that equilibration with soil CO_2 is unknown, and also to their use of temperatures estimated from the $\delta^{18}\text{O}$ of pedogenic calcite, which has not been rigorously calibrated for use in the paleo-record (Dworkin et al., 2005).

Several marine sections spanning the Late Triassic to Early Jurassic show evidence for a marked increase in basalt weathering product. Most notably, substantial fluctuations in the $^{187}\text{Os}/^{188}\text{Os}$ of seawater between ~ 203 -197 Ma are found in marine sections from St. Audrey's Bay, UK (Cohen and Coe, 2007), and the Kurusu section from Japan (Kuroda et al., 2010), an effect which is attributed to increased flux of unradiogenic ^{188}Os from the weathering of the CAMP (Cohen and Coe, 2007) (Fig. 4.6).

To explain this relative increase in ^{188}Os , Cohen and Coe (2007) conclude that perhaps as much as 50% of the estimated $3 \times 10^6 \text{ km}^3$ of basalt could have been removed in a 3 Myr window following the eruptions, a rate which is close to the current weathering rate of ocean island basalts (Gaillardet et al., 1999). This interpretation is also supported by 2- to 3-fold increases in Os and Re concentrations in the Kurusu section in Japan (Kuroda et al., 2010) that we correlate to the St. Audrey's Bay record via the $^{187}\text{Os}/^{188}\text{Os}$ peak in both, within the error allowed by the biostratigraphy (Ward et al., 2004). The relatively low $^{187}\text{Os}/^{188}\text{Os}$ ratio that occurs just after the initial CAMP eruptions indicates that unradiogenic ^{188}Os was a significant proportion of the weathering flux, and the subsequent slow $^{187}\text{Os}/^{188}\text{Os}$ increase suggests that the proportion of unradiogenic component progressively decreased as the highly weatherable CAMP silicate was consumed. This scenario is consistent with our uppermost pCO_2 estimate from the Portland formation, ~ 1.5 Myr after the last pCO_2 increase, which suggests the return of atmospheric pCO_2 to equilibrium levels following consumption of the CAMP basalts (Fig. 4.5). However, our scenario leaves the decrease in $^{187}\text{Os}/^{188}\text{Os}$ leading up to the initial CAMP eruptions unexplained.

4.8. Summary and Conclusion

This paper presents evidence for the short and long-term effects of the CAMP volcanism on early Jurassic pCO_2 from strata in the Hartford basin of Eastern North America. We use the pedogenic carbonate paleobarometer (Cerling, 1999) to confirm the findings of Schaller et al. (2011a) in the corollary Newark basin, and to test the million-year scale effect of the CAMP eruptions.

We find that the Hartford basin $p\text{CO}_2$ record is consistent with observations from the Newark basin, where a $p\text{CO}_2$ maximum is identified just after each volcanic episode (to levels around $\sim 4500 \pm 1200$ ppm). The significantly longer post-extrusive Portland Formation of the Hartford basin shows evidence of a fourth pulse of CO_2 (to 4500 ± 1200 ppm) about 240 kyr after the last lava recorded in the Eastern North American section. We contend that this increase in CO_2 is volcanic in origin and may be attributed to a fourth pulse of widespread magmatism not represented by lavas in the ENA section. Using the fourth Newark Group pulse of CO_2 , found 240 kyr after the Hampden Basalt, we revise the estimated CAMP duration as observed in the Eastern North American section to $\sim 840 \pm 60$ kyr.

The Portland Formation record also shows a rapid post-eruptive decrease in $p\text{CO}_2$ that reaches pre-eruptive background concentrations of $\sim 2000 \pm 700$ ppm by ~ 250 to 300 kyr, consistent with observations from the Newark basin. Furthermore, the longer Portland Formation exhibits a long-term decrease in $p\text{CO}_2$ over the subsequent 1.5 Myr following the final eruptive episodes, to levels below the pre-CAMP background. We use a geochemical model based on the COPSE code to demonstrate that the rapidity of the decreases, and the fall to concentrations below background can be accounted for by a 1.5-times amplification of the continental silicate weathering response due to the presence of the CAMP basalts themselves. If basalt has 10-times the reactivity of continental crust, such an amplification would require $\sim 8.3 \times 10^6 \text{ km}^2$ of basalt to be erupted, comparable to estimates for the areal extent of the CAMP at $1.12 \times 10^7 \text{ km}^2$ (McHone, 2003). This finding is generally corroborated by other modeling efforts showing a similar response of the carbon system to the emplacement of the Deccan Traps with 1.6×10^{18} moles CO_2

released over 100 kyr (Dessert et al., 2001). However, our result departs in that we achieve a more rapid response of the carbon system by releasing far less CO₂ (3.5×10^{17} moles) over an eruption time of 1000 years for any one of the CAMP extrusive units. A longer eruption time therefore would require significantly more CO₂ be released to achieve the same effect.

Together, these results indicate that continental flood basalts may result in an extreme short-term perturbation of the carbon system, followed by a long-term net-drawdown in pCO₂ to below pre-eruptive levels, implying that LIPs may have an overall net-cooling effect on climate through the connection between pCO₂ and temperature.

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Table 4.1: Samples from both outcrop and core from the Hartford basin

Sample	Core or Outcrop		Depth - below / +above Talcott Base (m)	Formation	Age (Ma) ^a	Down-profile mean $\delta^{13}C_{carb}$ (‰ PDB) ^b	$\delta^{13}C_{ox}$ (‰ PDB) ^c	Atmos. pCO_2 (ppm) (at $S_z = 3000 \pm 1000$ ppm)
	Lat	Lon						
HNH3-50	41.55649	-72.91159	-1200*	New Haven	211.9*	-7.4	-26.2	1775 ± 592
HNH2-47	41.55723	-72.91175	-1200*	New Haven	211.9*	-7.7	-26.4	1703 ± 568
HNH691B [†]	41.55956	-72.90775	-1175*	New Haven	211.9*	-7.2	-26.8	2218 ± 739
HNH691C [†]	41.55981	-72.90845	-1170*	New Haven	211.9*	-7.6	-26.9	2064 ± 688
HNHAAD [†]	41.39441	-72.8872	-500*	New Haven	~205	-7.6	-27.0	2065 ± 688
			0	Talcott Basalt	201.38			
HMSRB1-165	41.5850	-72.7565	120	Shurtle Meadow	201.26	-3.4	-26.2	5186 ± 1773
HSMAAA [†]	40.67295	-72.83597	200	Shurtle Meadow	201.18	-6.6	-26.0	3074 ± 1025
			241	Holyoke Basalt				
HEBFD26T-82	41.75863	-72.69509	540	East Berlin	200.84	-6.3	-26.2	2249 ± 746
			550	Hampden Basalt				
HPFD24T-112	41.75810	-72.693243	597	Portland	200.78	-4.6	-27.7	5473 ± 1824
HPFD24T-107	41.75810	-72.693243	599	Portland	200.78	-5.3	-26.1	2980 ± 993
HPFD24T-92	41.75810	-72.693243	603	Portland	200.77	-4.9	-26.2	3530 ± 1177
HPFD14T-82	41.75820	-72.690903	605	Portland	200.77	-3.0	-25.2	4391 ± 1464
HPFD20T-165	41.75792	-72.68815	631	Portland	200.75	-3.8	-25.2	4518 ± 1506
HPFD20T-99	41.75792	-72.68815	651	Portland	200.73	-3.6	-24.9	3574 ± 1191
HPFD16T-206	41.75791	-72.684209	671	Portland	200.71	-7.5	-27.8	2727 ± 909
HPFD16T-154	41.75791	-72.684209	686	Portland	200.69	-6.3	-27.2	3019 ± 1006
HPFD16T-126	41.75791	-72.684209	695	Portland	200.68	-7.1	-27.7	2811 ± 937
HPFD16T-48	41.75791	-72.684209	718	Portland	200.66	-4.8	-26.0	3455 ± 1152
HPFD13T-165	41.75763	-72.677278	726	Portland	200.65	-6.0	-26.7	2988 ± 996
HPFD22T-210	41.75776	-72.680457	744	Portland	200.63	-6.2	-27.1	3072 ± 1024
HPFD12T-210	41.75784	-72.675222	745	Portland	200.63	-5.8	-25.5	2317 ± 772
HPFD18T-138	41.75802	-72.682255	746	Portland	200.63	-4.9	-25.9	3280 ± 1093
HPFD12T-32	41.75784	-72.675222	799	Portland	200.58	-6.9	-26.6	2204 ± 735
HPFD19T-188	41.75768	-72.672524	801	Portland	200.58	-6.8	-27.0	2545 ± 848
HPFD23T-80	41.75771	-72.671683	847	Portland	200.53	-3.3	-25.5	4496 ± 1499
HPFD19T-32	41.75768	-72.672524	848	Portland	200.53	-4.6	-26.6	4125 ± 1375
HPFD30T-175	41.75734	-72.668001	913	Portland	200.46	-3.1	-25.7	5092 ± 1697
HPFD30T-86	41.75734	-72.668001	940	Portland	200.44	-5.9	-26.6	2882 ± 961
HPFD29T-185	41.75749	-72.664766	983	Portland	200.39	-5.6	-26.4	3003 ± 1001
HPFD29T-97	41.75749	-72.664766	1010	Portland	200.37	-7.3	-25.5	1496 ± 499
HPFD7T-101	41.75805	-72.664892	1025	Portland	200.35	-6.9	-26.4	2117 ± 706
HPFD27T-154	41.75751	-72.663522	1043	Portland	200.33	-5.7	-27.3	2649 ± 883
HPFD27T-94	41.75751	-72.663522	1062	Portland	200.31	-6.2	-26.6	2716 ± 905
HPFL [†]	41.5712	-72.6198	1143	Portland	200.23	-7.7	-26.0	1528 ± 509
HPFJ [†]	41.5723	-72.6163	1224	Portland	200.15	-9.3	-26.0	915 ± 305
HPJFA [†]	41.9747	-72.6598	1582	Portland	199.79	-9.5	-25.8	785 ± 262
HPJFEG [†]	41.9903	-72.5937	2379	Portland	198.99	-7.7	-26.6	1768 ± 589

† Samples from outcrop

* Depth estimate ± 200 m error, based on projection of the bedding dip. Age estimates from U/Pb date of 211.9 ± 2.1 Ma (Wang et al., 1998) on same/adjacent exposure

† Age based on cycle and magnetic stratigraphy tied to 201.38 absolute ages of first extrusive unit (Schoene et al., 2010)

† Analyzed on a Micromass Optima - dual inlet IRMS

† Analyzed on a Eurovector EA connected to VG Isoprime IRMS

4.10. Figures and Captions

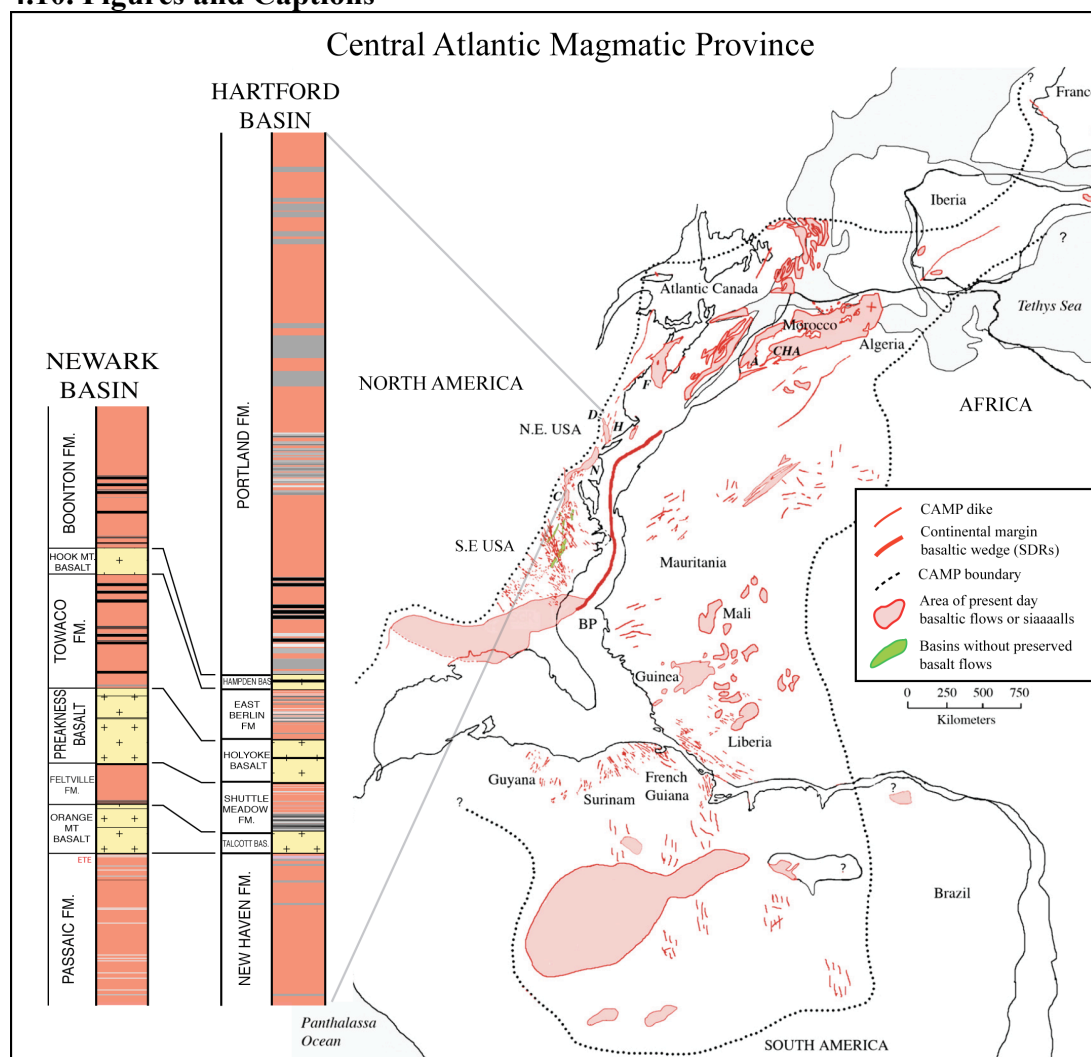


Figure 4.1: The distribution of the remaining CAMP volcanics and stratigraphy of the Newark and Hartford basins of Eastern North America (modified from Whiteside et al., 2007, which is based on McHone, 2000).

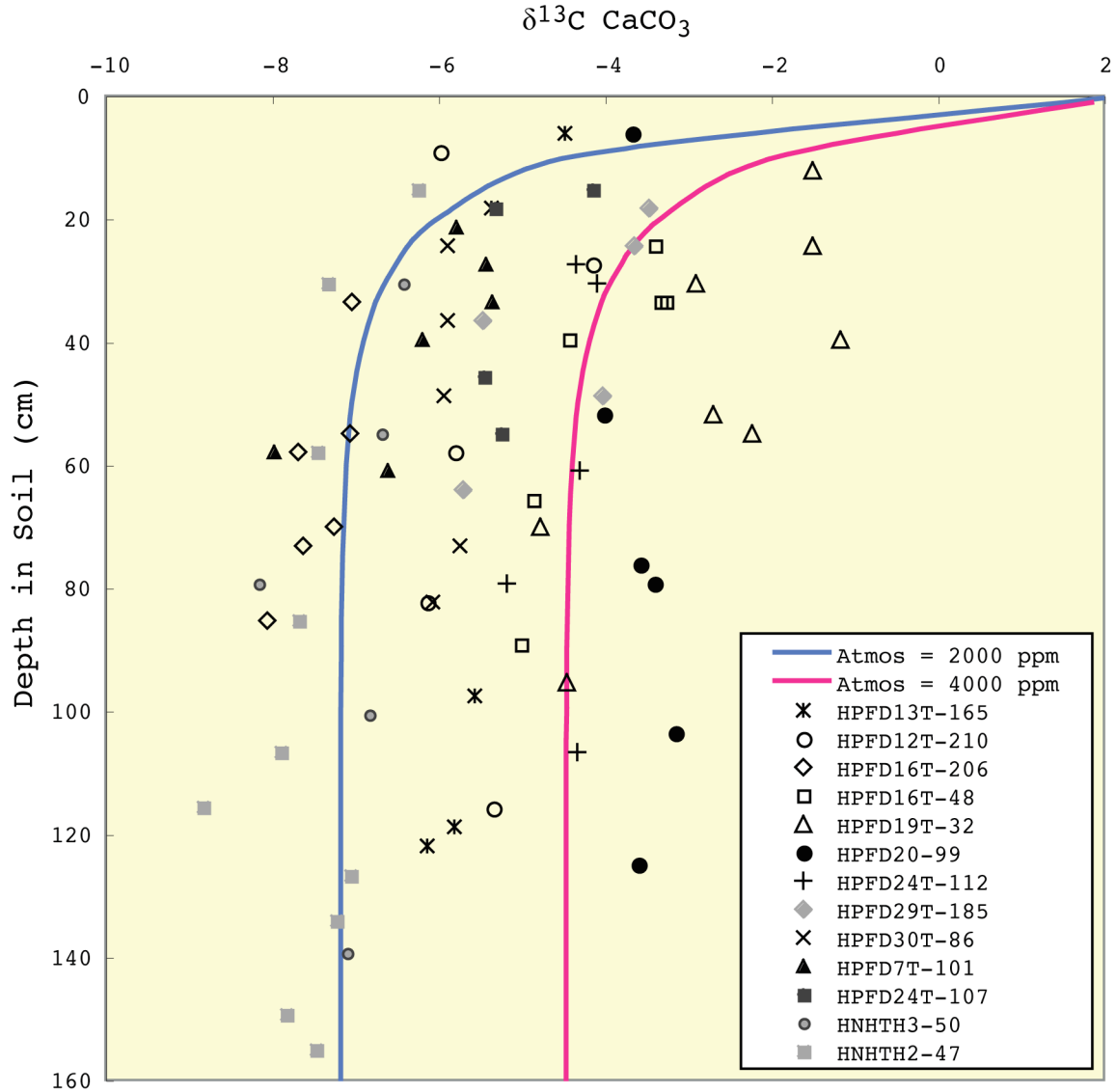


Figure 4.2: Stable carbon isotopic composition of pedogenic carbonate (δ_{cc}) with estimated soil depth from representative paleosols in the Portland Formation (symbols encompass analytical error). Note that these shallowest nodules represent depths to the uppermost carbonate nodules, which should not be confused with depth to the Bk horizon (Retallack, 2009). Observed δ_{cc} is compared to the δ_{cc} values predicted by the diffusion model at atmospheric CO_2 concentrations of 2000 ppm (blue line) and 4000 ppm (pink line) (after Quade et al., 1989). For this demonstration only, atmospheric $\delta^{13}\text{CO}_2$ was set to -6.5‰ , soil $\delta^{13}\text{C}_{\text{org}}$ was set to -26.5 , with an exponential production function and characteristic depth of production at 15 cm (other parameters described in text). For all $p\text{CO}_2$ estimates made in this study, the $\delta^{13}\text{C}_{\text{org}}$ was measured directly and used as a model input. Soil carbonate above 20cm in the profile was rare; note that stabilization of measured δ_{cc} is commonly well below 50cm soil depth. Only the mean of the equilibrium δ_{cc} values were used to calculate $p\text{CO}_2$ in this study.

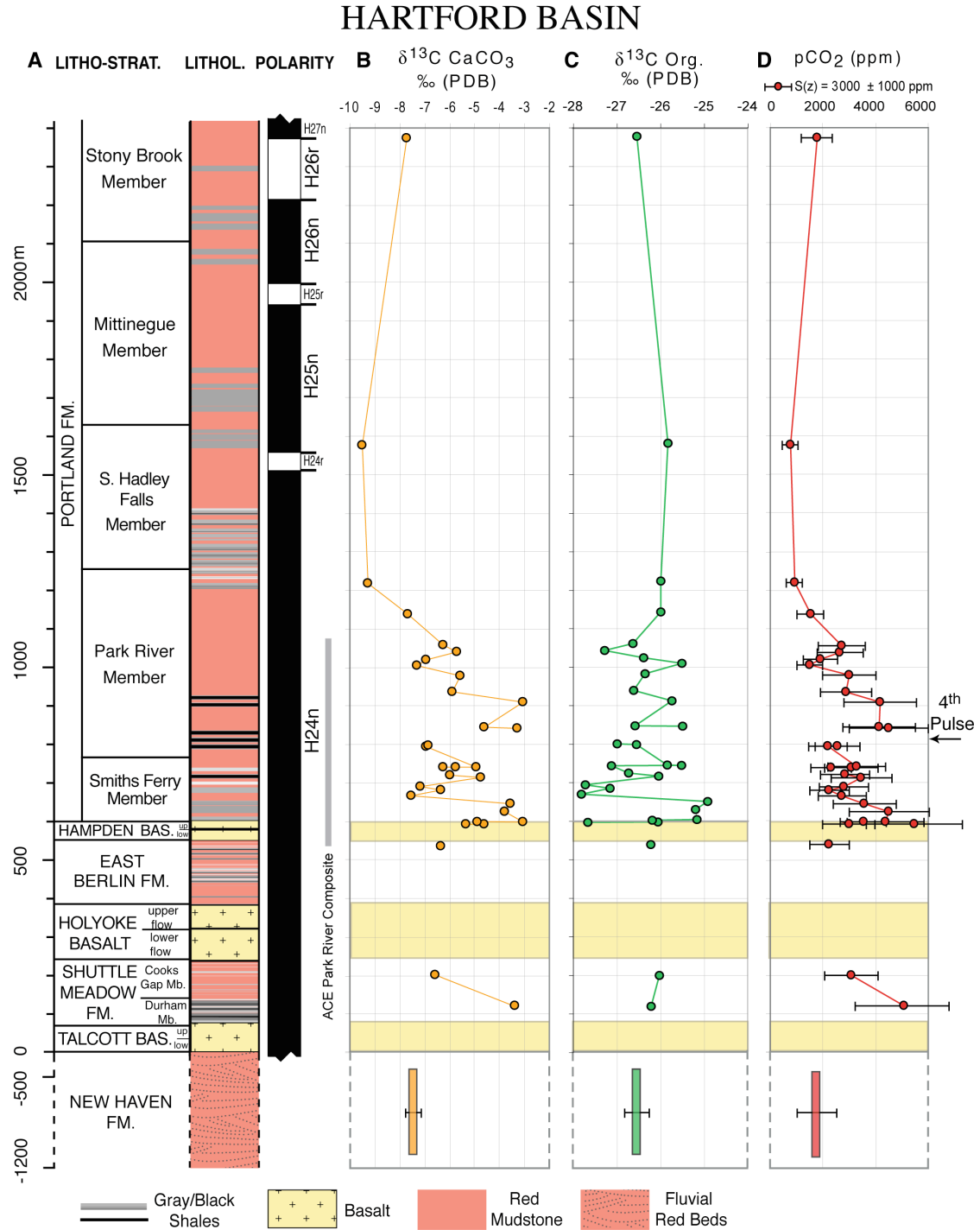
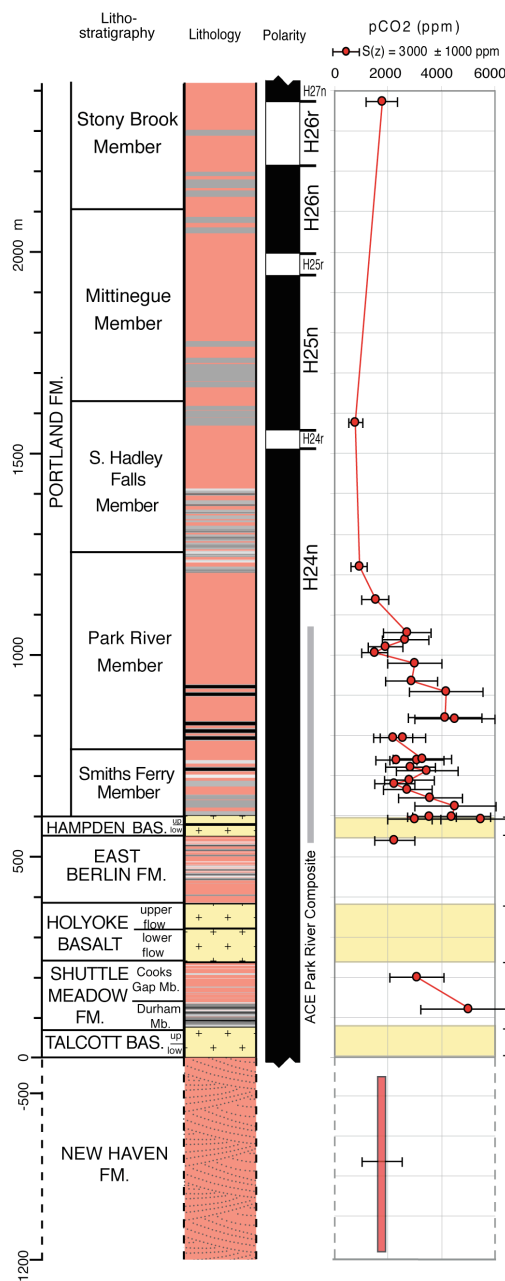


Figure 4.3: **A.** Lithologic and polarity stratigraphy of the Hartford basin from Kent and Olsen (2008). **B.** Profile equilibrated mean $\delta^{13}\text{C}$ values of pedogenic carbonate. **C.** $\delta^{13}\text{C}$ of organic matter from as close to the paleosol surface as possible. **D.** Calculated pCO_2 based on input variables in B and C at 25°C. The concentration of respired CO_2 in the soil $[\text{S}(z)]$ was estimated at 3000 ± 1000 ppm, and the resulting range of pCO_2 is indicated by the $\pm$ error bars on each estimate. For B, C, and D, only the mean $\pm$ standard

deviation of the 5 sample locations from the New Haven Formation is shown because of stratigraphic uncertainty; see Table 1 for depths below the Talcott Basalt.

HARTFORD BASIN



NEWARK BASIN

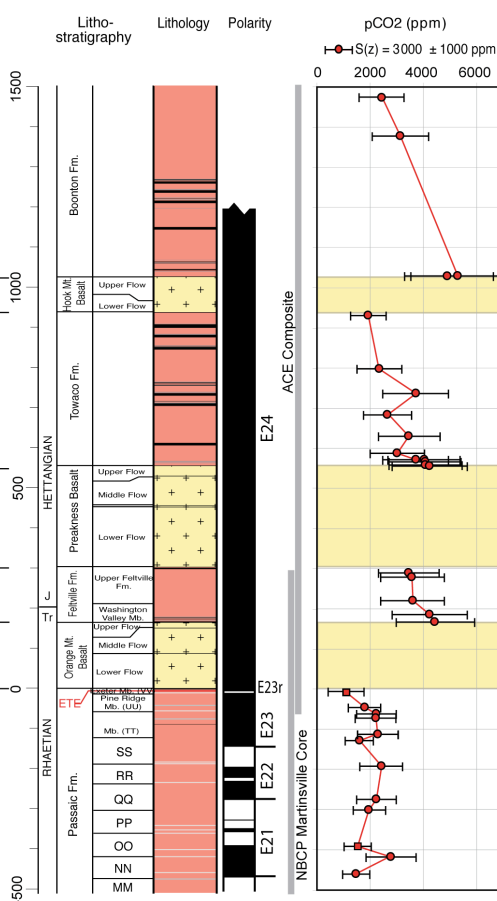


Figure 4.4: Calculated pCO₂ from the Hartford basin compared to the Newark basin pCO₂ record of Schaller et al (2011a). Error bars represent calculated pCO₂ at soil respired CO₂ concentrations [S(z)] of 3000 ± 1000 ppm. The Army Corps of Engineers (ACE) suite of Park River cores is denoted by gray bar in the Hartford basin, covering the lower Portland Formation in high resolution. For comparison to the pre-CAMP background of Schaller et al (2011), samples from the New Haven Formation are shown as a mean of the pCO₂ estimates between ~500 m and ~1200 m below the Talcott Basalt (see Table 1), with an error corresponding to S(z) values of 3000 ± 1000 ppm.

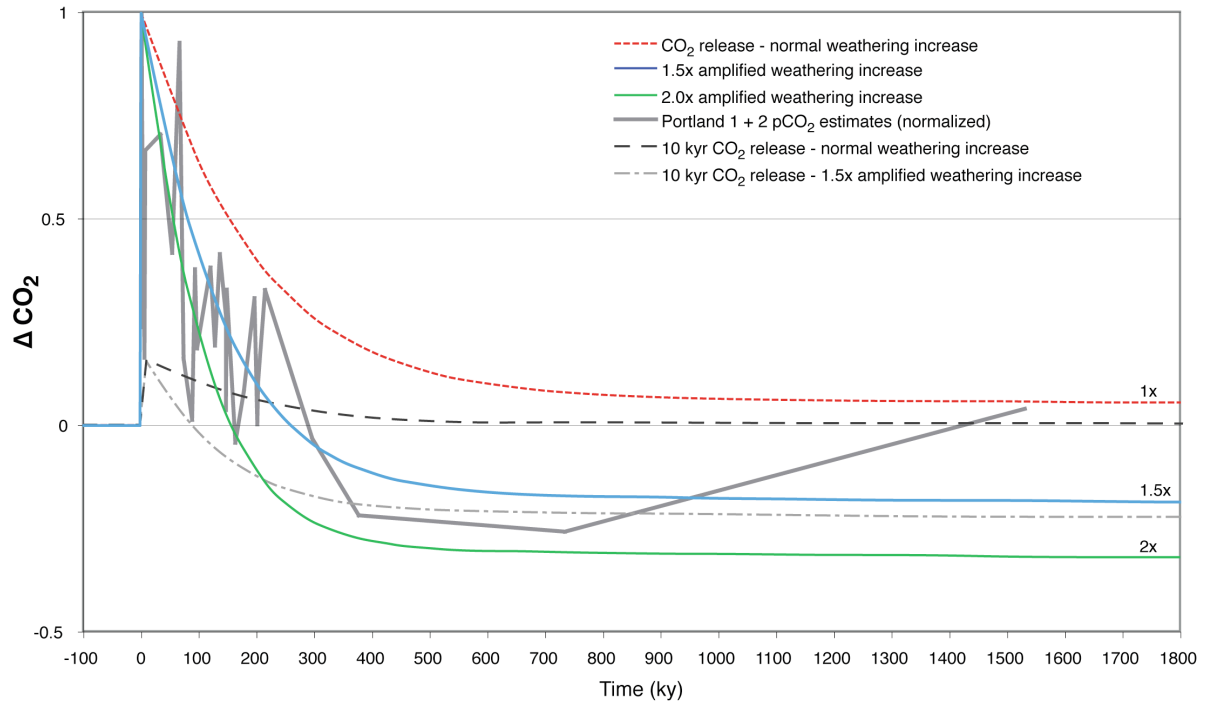


Figure 4.5: The pCO₂ record of the post-extrusive Portland Formation (at S(z) = 3000 ppm) (gray line), normalized to their respective increases above background, combined with one another, and scaled to an initial eruptive pulse at t = 0, for comparison to the results of geochemical modeling using a modified version of the COPSE model (Bergman et al., 2004). The model equilibrates the atmosphere and ocean on the 1000-year timescale. In the reference run (red dotted-line), the model achieves steady state for 100 kyr, at which point atmospheric CO₂ was doubled over 1000 years (by adding 3.5×10^{17} moles of CO₂) to simulate the eruption of a single pulse of CAMP volcanics and their CO₂ release. The ensuing decrease in pCO₂ is due to consumption by increased continental weathering rate resulting from the high pCO₂ and resultant increased temperatures. In the test simulations, the ocean-atmosphere CO₂ reservoir was again doubled in size, while the increased rate of silicate weathering was concordantly further amplified by 1.5- (blue line) and 2-times (green line), in an attempt to simulate the effects of freshly erupted basalts on the continental weathering budget. A second set of test simulations shows the effect of the same CO₂ pulse released over 10 kyr without an amplification of the weathering increase (black dashed line), and with a 1.5x amplification (gray dot-dash line). The model was run for a total of 1.9 Myr. Linear correlation of each 1000-year release simulation to the observed normalized Portland pCO₂ estimates at S(z) = 3000 ppm (using least-squares) gives $R^2 = -0.03$ for the reference simulation, $R^2 = 0.62$ for the 1.5-times amplification of the weathering increase, and $R^2 = 0.46$ for the 2-times amplification.

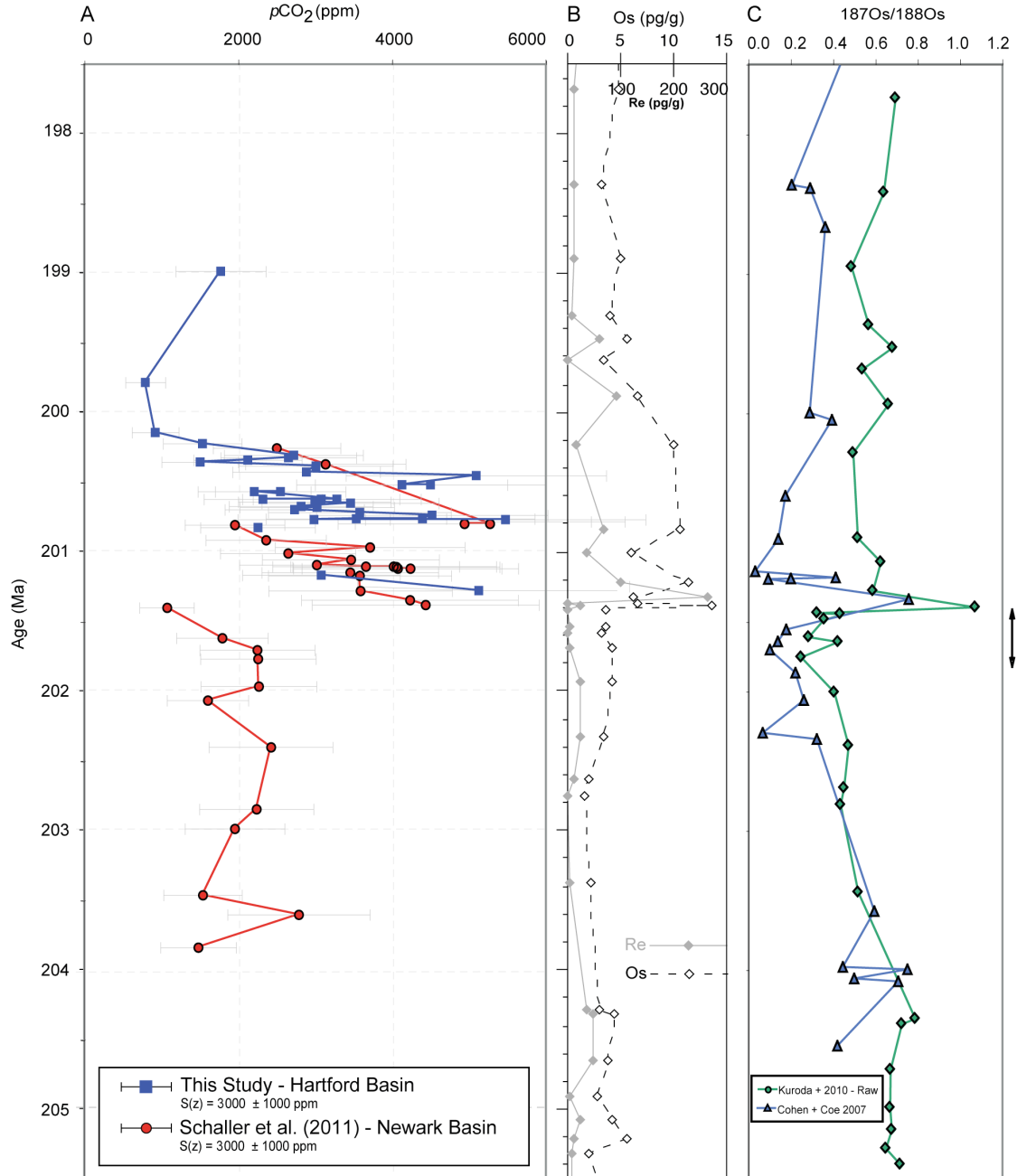


Figure 4.6: **A.** Composite Newark and Hartford $p\text{CO}_2$ record of this study. Newark data are from Schaller et al. (2011). **B.** The [Os] and [Re] records from the Kurusu section in Japan, plotted using the accumulation rates of Kuroda (2010), with the record correlated using the peak in $^{187}\text{Os}/^{188}\text{Os}$ to the corresponding $^{187}\text{Os}/^{188}\text{Os}$ peak in the isotope record of Cohen and Coe (2007). (note difference in Re and Os scales). **C.** $^{187}\text{Os}/^{188}\text{Os}$ ratios from the Kurusu section in Japan (Kuroda et al., 2010) and the St. Audrey's Bay, U.K (Cohen and Coe, 2007). Here we have used the peak in $^{187}\text{Os}/^{188}\text{Os}$ in St. Audrey's Bay (Cohen and Coe, 2007) as a marker for a more appropriate correlation to the Kurusu section (contra Kuroda et al., 2010), which is afforded by the error in biostratigraphy and the residence time of Osmium in the oceans (Oxburgh, 2001). Placement offset noted by arrow.

Chapter 5

A 33 million-year record of Late Triassic pCO₂ reflects fundamental control of the carbon-cycle by changes in continental distribution⁴

5.1. Abstract

A ~33 My continuous record of pCO₂ spanning the Late Triassic to Earliest Jurassic, based on paleosols from the eastern North American Newark rift basin, shows high pCO₂ values near 4500 ± 1400 ppm (at $S(z) = 3000 \pm 1000$ ppm) in the late Carnian, decreasing to $\sim 2000 \pm 700$ ppm by the late Rhaetian, just before the eruption of the Central Atlantic Magmatic Province. These data are consistent with the model results of Godderis et al. (2008), who predict falling pCO₂ through the Late Triassic as a result of the progressive increase in continental area in the tropical humid belt due to Pangea's slow northward transect. In detail, pCO₂ in the Newark corresponds closely to the rate of Northward movement of the Pangean supercontinent, as determined from paleolatitude reconstructions on the Newark Basin Coring Project Cores. These observations are more compatible with a weathering-forced driver for long-term variability in atmospheric pCO₂ than with the BLAG hypothesis, where trends in pCO₂ are forced by changes in the rate of ocean crust production. Therefore, we contend that continental weathering rates, which are fundamental expressions of the composition and changing distribution of continental surface area, tightly control the 10⁷-year secular changes in pCO₂ observed in the Late Triassic. This leads us to conclude that paleogeography and the rates of change

⁴ Morgan F. Schaller, James D. Wright, Dennis V. Kent. In prep for submission to *Geology*, January 2012.

in continental distributions (and lithology) could be the primary driver of Earth's climate on long timescales.

5.2. Introduction

On the million-year scale, equitable climates at Earth's surface are controlled primarily by a balance between the CO₂ outgassed at mid-ocean ridges and other volcanoes, and the consumption of that CO₂ by weathering reactions on the continents. Because CO₂ exerts a fundamental control over temperature, and temperatures influence precipitation patterns (Manabe and Wetherald, 1980), and determines the rate constants in continental hydrolysis reactions (see Kump et al., 2000, for review), an increase in atmospheric pCO₂ ultimately leads to an increase in chemical weathering. Increased weathering more rapidly consumes CO₂, leading to an eventual decrease in atmospheric pCO₂, thus constituting a 'thermostat' that keeps Earth's temperature within a stable range (Walker et al., 1981). One way to tip the balance in this relationship is to change the rate of CO₂ degassed from Earth's mantle. This perspective has led to a generation of carbon cycle mass-balance models (e.g., BLAG and GEOCARB (Berner, 1990; Berner et al., 1983)) that force long-term (geologic scale) changes in pCO₂ by the cumulative effects of transient changes in the rate of degassing at mid-ocean ridges, treating the weathering consumption of atmospheric CO₂ as a simple feedback response (Berner, 1991).

Such source-side processes have dominated attempts to explain the evolution of atmospheric pCO₂ on timescales like the Phanerozoic, with the only substantial suggested sink-side perturbations thought to be related to uplift during massive orogenic

reorganizations (e.g., Raymo and Ruddiman, 1992). However, this simplified view of the system does not account for tectonic-scale changes in the distribution of continental area with respect to the zones on earth's surface where weathering is most active (Godderis et al., 2008), or the relocation or eruption of highly weatherable material into the equatorial humid belt (Dessert et al., 2001; Kent and Muttoni, 2008; Schaller et al., 2011b). These alternate explanations for the 10^6 to 10^7 -year scale $p\text{CO}_2$ variability constitute sink-side processes due to the spatial, temporal and lithologic heterogeneity of continental surface participation in weathering reactions, which are independent of changes in mid-ocean ridge degassing. This paper focuses specifically on the evolution of atmospheric $p\text{CO}_2$ and how it was influenced by the changing distribution of continental area in the late Triassic.

Godderis et al. (2008) predict that the northward migration of Pangea through the Triassic into the Jurassic resulted in a two-thirds reduction in atmospheric $p\text{CO}_2$ by the latest Triassic, due to the steady increase in the amount of weatherable land area present in the tropical humid belt. Their approach departs from more simplified mass-balance calculations because they account for the effects of dramatic changes in paleogeography, leading them to conclude that the distribution of continental area must be a primary driver of long-term $p\text{CO}_2$ trends.

We test this hypothesis empirically by reconstructing atmospheric $p\text{CO}_2$ from the 33 Myr continuous section of Late Triassic provided by the continental strata of the Newark rift basin in eastern North America. We employ the pedogenic carbonate paleobarometer (Cerling, 1999), which uses the stable carbon isotope ratios of the organic and inorganic phases of fossil soils as a proxy for atmospheric $p\text{CO}_2$ at the time of

formation. Paleosols from these strata were used successfully to estimate the transient atmospheric $p\text{CO}_2$ perturbation associated with the Central Atlantic Magmatic Province (Schaller et al., 2011a), which sits toward the top of the Newark basin section. Here we present data from the underlying ~4500 m of section, showing a secular decrease in $p\text{CO}_2$ from the Carnian to the Rhaetian, which we propose is a function of the amount and rate at which continental area is moved into the equatorial humid belt, where atmospheric CO_2 is most efficiently consumed.

5.2.1. The Newark Basin

The majority of the samples used in this study are taken from a series of long cores through the sedimentary strata of the Newark rift basin in eastern North America acquired by the Newark Basin Coring Project (NBCP) (Kent et al., 1995; Olsen et al., 1996a). Sediments filling this half-graben basin are comprised of shallow to deep lacustrine, fluvial, alluvial and playa facies (Olsen, 1997; Smoot, 1991), deposited in tropical latitudes (Kent et al., 1995; Kent and Tauxe, 2005); these strata dip toward the main border fault to the northwest. The seven individual NBCP cores comprise a complete and continuous ~5000 m composite stratigraphic section, spanning the mid-Carnian of the Late Triassic to the Hettangian of the Early Jurassic (Fig. 5. 1). The boreholes (stratigraphically upward: Princeton, Nursery, Titusville, Rutgers, Somerset, Weston Canal, and Martinsville) were spudded for maximum overlap up-section, and from as close to the center of the basin as possible. However, even those cores that are ~50 km geographically disparate (e.g., the Rutgers and Titusville cores) show nearly identical stratigraphy within zones of overlap.

The lacustrine facies are ordered in a rhythmic succession reflecting periodic fluctuations in lake depth (Van Houten, 1962), and have been related directly to Milankovitch orbital forcing of tropical precipitation (Olsen, 1986; Olsen and Kent, 1996). This record of orbitally forced sedimentation provides the astronomical chronometer used to construct the geomagnetic polarity time scale for more than 33 Myr of the Late Triassic and Early Jurassic (Kent and Olsen, 1999; Kent et al., 1995; Olsen and Kent, 1996, 1999). The tholeiitic basalts of the Central Atlantic Magmatic Province are present near the top of the stratigraphic sequence, and provide the crucial radiometric age control to which the astrochronology is tied (Olsen and Kent, 1996; Olsen et al., 1996a). The most precise Ur-Pb dates place the first eruptive units at 201.38 ± 0.31 Ma (total analytical and calibration error) (Schoene et al., 2010), while $^{40}\text{Ar}/^{39}\text{Ar}$ ages center around 201 Ma (e.g., Hames et al., 2000; Jourdan et al., 2009).

5.3. pCO₂ estimates from pedogenic carbonates

Pedogenic carbonate nodules were collected from paleosols distributed throughout the Newark basin section, primarily from the NBCP cores, and also from select exposures elsewhere in the basin. Samples from the upper portion of the Martinsville core were used to establish pre-CAMP background pCO₂ levels by Schaller et al. (2011a), and samples from a series of short geotechnical cores taken by the Army Corps of Engineers (ACE) covers the extrusive interval. Section-depths are translated to time using the astronomically determined NBCP chronostratigraphy (Kent and Olsen, 1999; Kent et al., 1995; Olsen and Kent, 1996; Olsen et al., 1996a), which provides tight age control, making these pCO₂ estimates both temporally precise and globally relevant.

Organic and inorganic carbon isotope measurements from these paleosols were used to estimate C_a , the concentration of atmospheric CO_2 , according to the soil diffusion model of Cerling (1999):

$$C_a = S(z) \frac{\delta_s - 1.0044\delta_\phi - 4.4}{\delta_a - \delta_s} \quad (\text{Eqn. 1})$$

where, $S(z)$ is the concentration of CO_2 at soil depths greater than 50cm contributed by the respiration of soil organic matter, δ_s is the $\delta^{13}\text{C}$ of soil CO_2 , δ_ϕ is the $\delta^{13}\text{C}$ of soil-respired CO_2 , and δ_a is the $\delta^{13}\text{C}$ of atmospheric CO_2 . All δ values are relative to Vienna PeeDee Belemnite (VPDB).

The carbon isotopic ratio of soil carbonate (δ_{cc}) is used as a proxy for δ_s , which involves a temperature-dependent equilibrium fractionation between CaCO_3 and CO_2 , described by:

$$10^3 \ln \alpha = 11.709 - 0.116(T) + 2.16 \times 10^{-4} (T)^2 \quad (\text{Cerling, 1999})$$

where α is the fractionation factor, and temperature (T , in $^\circ\text{C}$) is fixed at 25°C , as appropriate for the tropical Newark basin. Because there is no carbon isotope fractionation due to respiration, δ_ϕ is related directly to the carbon isotopic ratio of soil organic matter ($\delta^{13}\text{C}_{\text{org}}$). The carbon isotopic ratio of the atmosphere is calculated from the measured $\delta^{13}\text{C}_{\text{org}}$ by the following relationship (Arens et al., 2000):

$$\delta_a = (\delta^{13}\text{C}_{\text{org}} + 18.67)/1.10$$

which assumes consistent fractionation by photosynthesis. This builds carbon-cycle perturbations directly into the model. The only adjustable parameter of the model is the concentration of CO_2 in the soil derived from the respiration of organic matter ($S(z)$), which is a function of soil productivity. The paleosols sampled in this study were relatively productive argillic and vertic calcisols (Mack et al., 1993), with mean depth to

the Bk horizon (D_s) at 40 ± 15 cm soil depth, which we use to estimate $S(z)$ by the following empirical relationship: $S(z) = 66.7D_s + 588$ (Retallack, 2009). This results in a mean $S(z)$ of ~ 3256 with an empirical standard error of $SE = \pm 893$ ppm (Retallack, 2009). Given the difficulty inherent in accurately estimating depth to the Bk horizon in individual paleosols from drill cores, and in accordance with the work of Breecker et al. (2009a, 2010), we use an $S(z)$ value of 3000 ± 1000 ppm for all pCO_2 estimates, which gives a final pCO_2 range that is indistinguishable from the error that would result from systematic use of the empirical depth to carbonate relationship. Individual soil profiles were not decompacted (Retallack, 2009), and our $S(z)$ approximations are therefore conservatively low.

A combination of thin sections and polished slabs are used to identify primary micritic calcite from diagenetic material (Driese and Mora, 2002), with a sampling preference for small, isolated carbonate nodules that are generally in better isotopic equilibrium with the surrounding soil than larger nodules or calcretes (Schaller et al., 2011a). Great care was taken to avoid phreatic calcretes, and to sample only those displaying clear evidence of having formed in the vadose zone (Rasbury et al., 2006). Samples for organic carbon isotope analysis were taken from as close to the soil-surface as possible to avoid measuring recalcitrant organics unrelated to the active organic carbon pool during soil formation (Nadelhoffer and Fry, 1988), and several samples from each profile were homogenized to provide a more representative organic carbon value.

The $\delta^{13}C$ value of pedogenic carbonate is known to decrease predictably with soil depth (Quade et al., 1989), and characterizing this trend makes it possible to differentiate between the relative influences of the atmospheric vs. soil-respired CO_2 reservoirs.

Therefore, multiple (at least 5) down profile isotopic measurements were made on each paleosol to identify an equilibrium δ_{cc} value with depth in the soil (Schaller et al., 2011a) (Fig. 5.2). Using the mean of these depth-controlled measurements ensures that the mixing between the atmospheric and soil-respired reservoirs is at equilibrium with respect to the diffusion model, removing significant uncertainty in the isotopic maturity of a given paleosol profile.

5.4. Results

In the Stockton Formation, the oldest strata covered by the NBCP-core composite, $\delta^{13}\text{C}$ values from pedogenic carbonates in the Princeton core show an increase from ~ -5 ‰ at the base of the section, to ~ -3 ‰ near the top of the Stockton (Fig. 5.3, See Table 5.1 for all values). Values from the bottom of the Nursery core confirm those in the uppermost Stockton, which are followed by an increase from ~ -2.7 ‰ at the base of the Lockatong Formation to ~ -1.7 ‰ at its top in the Nursery core. Stable isotope ratios of organic carbon follow a very similar pattern: -27 ‰ in the base of the section in the Stockton Formation, increasing to -23 ‰ at the top of the Lockatong Formation. These values translate to $p\text{CO}_2$ concentrations that are variable around $\sim 4000 \pm 1200$ ppm from the Stockton Formation to the top of the Lockatong Formation (Fig. 5.3).

Calcic soils are largely absent from the lowermost Passaic Formation in the Titusville core, but appear in abundance at the top of the Titusville and base of the Rutgers cores, which overlap each other by ~ 200 m (Fig. 5.3). Here the $\delta^{13}\text{C}$ of pedogenic carbonate in both cores decreases sharply to around -4 ‰ at 2200 m section depth, before returning to values around -2 ‰. The $\delta^{13}\text{C}$ of organic matter follows a very

similar pattern, decreasing from -22 ‰ to -26.5 ‰, settling at -25 ‰. Atmospheric $p\text{CO}_2$ calculated from these values increases sharply from $\sim 4000 \pm 1200$ ppm, to 5500 ± 1700 ppm at 2100 m, decreasing to about 3000 ± 1000 ppm through the Rutgers core to 1500 m section depth. All measured isotope values and calculated $p\text{CO}_2$ concentrations show a very tight correspondence in the ~ 200 m interval of overlap between the Rutgers and Titusville cores, despite being located ~ 50 km from one another across the basin (Table 5.1, Fig. 5.1).

Around 1500 m section depth, the $\delta^{13}\text{C}$ of pedogenic carbonate begins a trend from -3 ‰ at the top of the Rutgers and base of the Somerset cores, through Weston Canal core, to -7 ‰ in the Martinsville core at ~ 100 m section depth (Fig. 5.3). The $\delta^{13}\text{C}$ of organic matter follows a similar trend from -23 ‰ to -27 ‰. Atmospheric $p\text{CO}_2$ calculated from these values shows an increase to $\sim 4500 \pm 1400$ ppm at ~ 1200 m, followed by a secular decline to $\sim 2000 \pm 700$ ppm just below the base of the Orange Mountain Basalt.

In the broadest chronostratigraphic sense, $p\text{CO}_2$ follows a trend from $\sim 4500 \pm 1400$ ppm in the late Carnian at around ~ 228 Ma, decreasing to around $\sim 2000 \pm 700$ ppm in the late Rhaetian at ~ 202 Ma, just before the CAMP eruptions (Fig. 5.4). The observed second-order $p\text{CO}_2$ changes may be summarized to a few distinct trends. From 233 to 215 Ma, $p\text{CO}_2$ remains relatively constant around $\sim 4500 \pm 1400$ ppm. After a slight spike to $\sim 5000 \pm 1600$ ppm at 215 Ma, we observe a ~ 4 Myr secular decrease to $\sim 2000 \pm 700$ ppm, at ~ 211 Ma. Comparable atmospheric $p\text{CO}_2$ concentrations are also found at this level in the Hartford basin (Schaller et al., 2011b), 250 km to the north, from exposures in the New Haven Formation dated to $\sim 211.9 \pm 2.1$ Ma by U-Pb on pedogenic

calcretes (Wang et al., 1998). A 3-Myr increase to a final $p\text{CO}_2$ maxima at 209 Ma of 4500 ± 1400 ppm is followed by an 8-Myr secular decrease to $\sim 2000 \pm 700$ ppm, just before the CAMP eruptions.

Our findings from the Newark basin are broadly comparable to paleosol-based $p\text{CO}_2$ estimates from elsewhere over the same ~ 33 Myr interval (Fig. 5). Our observations are particularly consistent with the general decreasing trend in $p\text{CO}_2$ estimates made from plant stomata (compiled from McElwain et al. (1999) and Retallack (2001)), with estimates of >4000 ppm in the late Carnian, falling to ~ 1000 ppm in the Rhaetian. Stomata-based $p\text{CO}_2$ estimates tend to be lower than those made from pedogenic carbonates, but the relative changes (at least in the Triassic/Jurassic) often mimic one another (e.g., Schaller et al., 2011a; Schaller et al., 2011b), which indicates they are tracking the same signal. Estimates of $p\text{CO}_2$ from pedogenic carbonates elsewhere through the Triassic are particularly variable (Fig. 5.5), with those from the older literature often using unrealistic unrealistically high $S(z)$ values (Breecker et al., 2009b; Ekart et al., 1999), and more recent attempts hampered by recalcitrant organic matter and a lack of soil-depth controlled equilibrium $\delta^{13}\text{C}$ values (Cleveland et al., 2008). Nonetheless, the mean of these estimates is at least similar to the Rhaetian levels measured here.

We note that the general trend of increasing apparent aridity of facies up section in the Newark basin (Smoot, 1991) tends to favor soils that might have lower $S(z)$ values, because of a decrease in soil productivity and an increase in seasonal extremes (Breecker et al., 2009a). If this were the case, our use of a fixed $S(z)$ would increasingly bias the results toward higher final $p\text{CO}_2$ estimates with increasing aridity because a relatively

low (and decreasing) $S(z)$ predicts less influence of the isotopically light soil respired CO_2 reservoir on soil CO_2 . Instead, our $p\text{CO}_2$ estimates show the opposite trend up-section, which implies our parameterization scheme for $S(z)$ is reasonable, because decreasing $S(z)$ up-section would tend to exacerbate the observed decrease.

5.5. Pangea's northward drift creates a massive continental sink for CO_2

The most compelling feature of the Newark basin $p\text{CO}_2$ record is the long-term decrease from $\sim 4500 \pm 1400$ ppm in the late Carnian, to $\sim 2000 \pm 700$ ppm in the late Rhaetian (Fig. 5.4). Godderis et al. (2008) predict a very similar trend using the GEOCLIM model, which couples a carbon cycle mass-balance model to a 3D-climate model, estimating $p\text{CO}_2$ at >3000 ppm in the Carnian, falling to <1000 ppm in the Rhaetian. Unlike simpler mass-balance models, GEOCLIM includes the effects of changing paleogeography while holding mid-ocean ridge production (and hence, mantle CO_2 degassing) constant through the Late Triassic. This results in a 3-fold decrease in $p\text{CO}_2$ over the course of the Late Triassic as the Pangean supercontinent progressed northward (Kent and Tauxe, 2005), and because of continental geometry, increased the amount of continental area within the equatorial humid belt, which accounts for $\sim 70\%$ of modern silicate weathering (Gaillardet et al., 1999; Hilley and Porder, 2008). This northward progression, with a long-term average of 0.6° latitude per My, furnished a massive and relatively transient continental sink for CO_2 .

Mass-balance models such as GEOCARB III (Berner and Kothavala, 2001) or COPSE (Bergman et al., 2004), based on the BLAG hypothesis (Berner et al., 1983), are unable to produce these results in the Late Triassic (Fig. 5. 4). The major forcing of

pCO₂ change in these models is from the cumulative effects of changes in ocean crust production rates and accompanying CO₂ degassing, which can only be approximated over long timescales by inverting sea-level reconstructions from continental margins (e.g., Gaffin, 1987). However, the sea-level-based record of ocean crust production used in GEOCARB shows very little change in the Late Triassic (Gaffin, 1987), meaning there is virtually no pCO₂ forcing incorporated in the model. Consequently, the model produces a steady-state result, as if crustal production and attendant degassing were held in nearly constant balance (see Fig. 5. 4). Because of this happenstance, the output of GEOCARB can be compared directly to that of the Godderis et al. (2008) model in the Late Triassic, with the only effective difference between them being GEOCARB's lack of allowable sink-side forcing. This crucial difference leaves BLAG-based models incapable of producing a trend comparable to what we observe in the Newark, simply because this class of models cannot include the effects of a net relocation of land area from the sub-tropical arid belt to the humid tropics. Thus, our results are consistent with the hypothesis of Godderis et al. (2008), that 10⁷-year pCO₂ changes are more crucially due to the distribution and relocation of continental area, here represented by the Late Triassic increase in tropical land area due to Pangea's northward migration.

5.6. Dynamic forcing of pCO₂ by continental weathering

As discussed above, the Godderis et al. (2008) model essentially forces changes in atmospheric pCO₂ by changing the amount of continental area in the tropical humid belt, holding ocean crust production constant. Even in the Cenozoic, estimates of changes in crustal production are based on imprecise extrapolations for already-subducted ocean

crust (Kominz, 1984; Muller et al., 2008), and the age distribution of continental crust from 180 Ma to present gives no indication that constant spreading rates can be excluded (Rowley, 2002). Therefore, constant ocean crust production is the best working assumption, but necessitates that the 10-to-5-Myr scale (second-order) changes in $p\text{CO}_2$ must therefore be tightly linked to changes in total tropical area, more so than to any other single process. Ignoring for the moment the short-term ≤ 3 Myr) variability in the Newark record, we find that the general trend in $p\text{CO}_2$ corresponds tightly with mean paleolatitudes calculated from each NBCP core (Fig. 5.6), which are directly related to the latitudinal position of the Pangean supercontinent. Because the geometry of Pangea is such that its east-west extent increases substantially to the south of the mid-Norian equator, moving the entire continent northward imparts a drastic increase in the amount of area in the tropics. We suggest that the rate at which continental area moves into the intense tropical weathering zone dictates changes in $p\text{CO}_2$ to a high order.

In detail, the modest decrease in $p\text{CO}_2$ from ~ 232 Ma to 225 Ma coincides with rapid northward movement of the Pangean supercontinent between the time of deposition of strata in the Princeton and Nursery cores (Fig. 6). However, the magnitude of this difference may be slightly exaggerated due to differences in the inclination flattening characteristics of the more fluvial sediments in the Stockton Formation (Kent and Tauxe, 2005). The relatively stable $p\text{CO}_2$ levels from 225 Ma to 215 Ma coincide with little change in paleolatitude between the Nursery, Titusville or Rutgers cores, and hence reflect a period of relatively slow northward movement with little change in tropical continental area above that necessary to maintain a steady state with mantle outgassing. The 8-million year secular decrease in $p\text{CO}_2$ beginning around 209 Ma (Fig. 5.6)

corresponds to an acceleration of northward movement that occurred between the deposition of strata represented by the Somerset and Martinsville cores. This acceleration probably increased the rate at which fresh material was delivered to the equatorial humid belt from the arid subtropics, increasing the rate of CO₂ consumption and hence leading to a steady drawdown of atmospheric pCO₂. These observations closely link atmospheric pCO₂ to the increase in continental weathering, which can be closely approximated as a function of the rate of Pangea's northward movement because of the increasing east-west extent of the continental area moving northward (see Fig. 5.6).

The Sr isotope record from Tethyan marine carbonates (Fig. 5.5) (Cohen and Coe, 2007; Korte et al., 2003) shows relatively little change from ~225 to 211 Ma, which is consistent with the relatively small change in paleolatitude from the NBCP cores from which we infer little change in tropical land area (Fig. 5.6). However, the Sr isotope record gives compelling evidence for an increase in more continentally derived weathering products from 209 to 202 Ma (Fig. 5.5), with values around 0.7081, and decreasing toward more mantle derived values of 0.7077 after the rapid eruption of the CAMP. The inference of more continentally derived weathering product from ~209 to 202 Ma is particularly relevant because an accelerated movement of continental crust from the arid climate belts into the humid tropics is expected to greatly accelerate the global rate of chemical weathering since runoff has the greatest single effect on modern weathering rates (Gaillardet et al., 1999). Again, barring any unknown changes in crustal production rates, these observations are most consistent with the hypothesis of Godderis et al. (2008), and in a finer degree of detail than their model output.

Therefore, we suggest that continental weathering rates, which are fundamental expressions of the distribution and composition of continental surface area, might tightly control even the sub- 10^7 -year changes in $p\text{CO}_2$ observed in the Late Triassic. As an example, we can take the observed ~ 2000 ppm decrease in $p\text{CO}_2$ ($\sim 3.5 \times 10^{17}$ moles CO_2) between ~ 215 to 211.3 Ma (Figs. 5.4 and 5.6), and estimate the amount of continental area necessary to increase the CO_2 consumption rate by $\sim 9.5 \times 10^{10}$ mol/yr over that period. If we consider that modern silicate weathering of continental crust consumes CO_2 at a rate of 6.14×10^4 mol/ km^2 /yr (Gaillardet et al., 1999), then $\sim 1.5 \times 10^6$ km^2 of continental area would have to be rapidly introduced into the tropics, or an area equivalent to roughly three-quarters the size of modern day Greenland. This relatively rapid $p\text{CO}_2$ decrease (215 to 211 Ma) and subsequent increase (211 to 209 Ma) could be the result of a continental “jerk” of northward movement, rather suddenly increasing the amount of area in the tropics over ~ 1 myr. A jerk is not unreasonable considering that the majority of the continental migration apparently began around ~ 215 Ma onward (Fig. 5.6), and represents about 8° of movement as deduced from the mean core paleolatitudes, leading to rather rapid increases in equatorial continental area considering the zonal geometry of Pangea’s central extent (Fig. 5.6). It is also worth noting that 209 Ma was roughly the time of rift-to-drift transition in the southern North American basins (Schlische, 2003).

Alternatively, weathering of modern basaltic rocks consumes CO_2 at a rate of 5.96×10^5 mol/ km^2 /yr (Dessert et al., 2003), in which case only $\sim 1.6 \times 10^5$ km^2 of basaltic terrain would be necessary to draw down $p\text{CO}_2$ at the added rate of $\sim 9.5 \times 10^{10}$ mol/yr. That is roughly the area of small modern day volcanic islands such as Java or the entire

Hawaiian island complex. Something of this size could easily be moved into the active weathering zone with rapidity; however, the Sr isotope record does not reflect an increase in the relative proportion of mantle-derived weathering product at this time (Fig. 5.5).

Because the organic C-cycle is responsible for ~20% of Earth's readily exchangeable carbon (Berner, 1990), an alternative explanation for the second-order changes in $p\text{CO}_2$ could reflect variations the rate of organic carbon burial or exhumation. Fortunately, those should be apparent from the $\delta^{13}\text{C}$ of marine carbonate, and no significant changes are observed in the Tethys marine $\delta^{13}\text{C}$ record that correspond to changes in $p\text{CO}_2$ through this interval (Korte et al., 2005) (Fig. 5.5). In fact, the long-term $\delta^{13}\text{C}$ decrease from ~215 Ma to ~201 Ma suggests a decrease in organic matter burial, which would increase $p\text{CO}_2$, the opposite of our observations.

5.7. Conclusions

Our overall results are consistent with a weathering-forced driver for long-term changes in atmospheric $p\text{CO}_2$. The systematic ~3 to 4-fold decrease in $p\text{CO}_2$ we observe through the Late Triassic can be related directly to increased continental area in the humid tropics. Because runoff has the greatest single effect on global silicate weathering rates (Gaillardet et al., 1999), and moving land area from arid climate zones to the humid tropics is one of the largest gradients in precipitation, this newly introduced tropical land area is very effective at consuming atmospheric CO_2 . Similar secular changes in $p\text{CO}_2$ throughout Earth's history may be related to the distribution and composition of continental crust in the intense weathering zones at Earth's surface, with no need to invoke changes in MOR spreading rates. Consequently, paleogeography and the rates of

change in continental distributions (and lithology) may be the primary driver of Earth's climate on long timescales.

5.8. References

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NPSOM-2214	40.5517	74.6467	Somerset 1	Passaic	1538.84	210.613	-3.64	-25.36	3908.4	1302.8
NPSOM-2645	40.5517	74.6467	Somerset 1	Passaic	1673.81	211.423	-3.33	-23.19	2435.1	811.7
NPRUT-465	40.5883	74.4333	Rutgers 2	Passaic	1674.25	211.426	-3.11	-24.20	3354.9	1118.3
NPRUT-619	40.5883	74.4333	Rutgers 1	Passaic	1727.99	211.748	-4.71	-25.33	2913.4	971.1
NPRUT-1254	40.5883	74.4333	Rutgers 1	Passaic	1927.27	212.944	-2.12	-23.80	3953.4	1317.8
NPRUT-2597	40.5883	74.4333	Rutgers 1	Passaic	2290.27	215.122	-2.17	-24.80	5093.6	1697.9
NPRUT-2710	40.5883	74.4333	Rutgers 1	Passaic	2320.08	215.300	-1.74	-24.15	4827.1	1609.0
NPRUT-2808	40.5883	74.4333	Rutgers 1	Passaic	2345.93	215.456	-3.32	-25.72	4698.5	1566.2
NPRUT-3082	40.5883	74.4333	Rutgers 1	Passaic	2409.72	215.838	-2.74	-24.20	3705.3	1235.1
NPTIT-148	40.3750	74.8533	Titusville 1	Passaic	2237.87	214.807	-2.42	-24.84	4791.5	1597.2
NPTIT-192	40.3750	74.8533	Titusville 1	Passaic	2246.50	214.859	-2.63	-24.93	4631.7	1543.9
NPTIT-245	40.3750	74.8533	Titusville 1	Passaic	2256.90	214.921	-2.48	-24.82	4684.8	1561.6
NPTIT-358	40.3750	74.8533	Titusville 1	Passaic	2279.07	215.054	-1.94	-24.89	5583.6	1861.2
NPTIT-652	40.3750	74.8533	Titusville 1	Passaic	2343.60	215.442	-3.91	-26.32	4670.4	1556.8
NPTIT-750	40.3750	74.8533	Titusville 1	Passaic	2363.68	215.562	-2.41	-24.88	4860.9	1620.3
NPTIT-1174	40.3750	74.8533	Titusville 1	Passaic	2444.37	216.046	-0.19	-21.95	4150.5	1383.5
NLNUR-457	40.3050	74.8617	Nursery 1	Lockatong	2774.80	218.029	-1.07	-23.40	4774.9	1591.6
NLNUR-837	40.3050	74.8617	Nursery 1	Lockatong	2874.10	218.625	-1.35	-23.22	4198.0	1399.3
NLNUR-2959	40.3050	74.8617	Nursery 1	Lockatong	3471.47	222.209	-1.94	-24.13	4534.0	1511.3
NSNUR-3302	40.3050	74.8617	Nursery 1	Stockton	3608.32	223.030	-3.27	-25.00	3941.0	1313.7
NLPRIN-602	40.3817	74.6817	Princeton	Lockatong	3407.98	221.828	-2.69	-24.54	4098.1	1366.0
NLPRIN-749	40.3817	74.6817	Princeton	Lockatong	3457.69	222.126	-2.68	-23.90	3487.4	1162.5
NSPRIN-1391	40.3817	74.6817	Princeton	Stockton	3801.40	224.188	-3.44	-25.74	4563.1	1521.0
NSPRIN-1779	40.3817	74.6817	Princeton	Stockton	4045.40	225.652	-3.51	-25.13	3821.2	1273.7
NSPRIN-1897	40.3817	74.6817	Princeton	Stockton	4108.68	226.032	-3.60	-26.22	4953.6	1651.2
NSPRIN-2021	40.3817	74.6817	Princeton	Stockton	4176.01	226.436	-3.90	-26.40	4773.9	1591.3
NSPRIN-2178	40.3817	74.6817	Princeton	Stockton	4261.27	226.948	-3.64	-26.54	5352.2	1784.1
NSPRIN-2409	40.3817	74.6817	Princeton	Stockton	4620.96	229.106	-4.17	-26.84	4979.6	1659.9
NSPRIN-2585	40.3817	74.6817	Princeton	Stockton	4700.05	229.580	-4.56	-26.07	3668.4	1222.8
NSPRIN-3067	40.3817	74.6817	Princeton	Stockton	4916.63	230.880	-5.32	-26.98	3774.6	1258.2
NSPRIN-3217	40.3817	74.6817	Princeton	Stockton	4984.03	231.284	-4.16	-26.72	4846.3	1615.4
NSPRIN-3440	40.3817	74.6817	Princeton	Stockton	5084.23	231.885	-3.59	-24.54	3214.2	1071.4

5.9. Figures and Captions

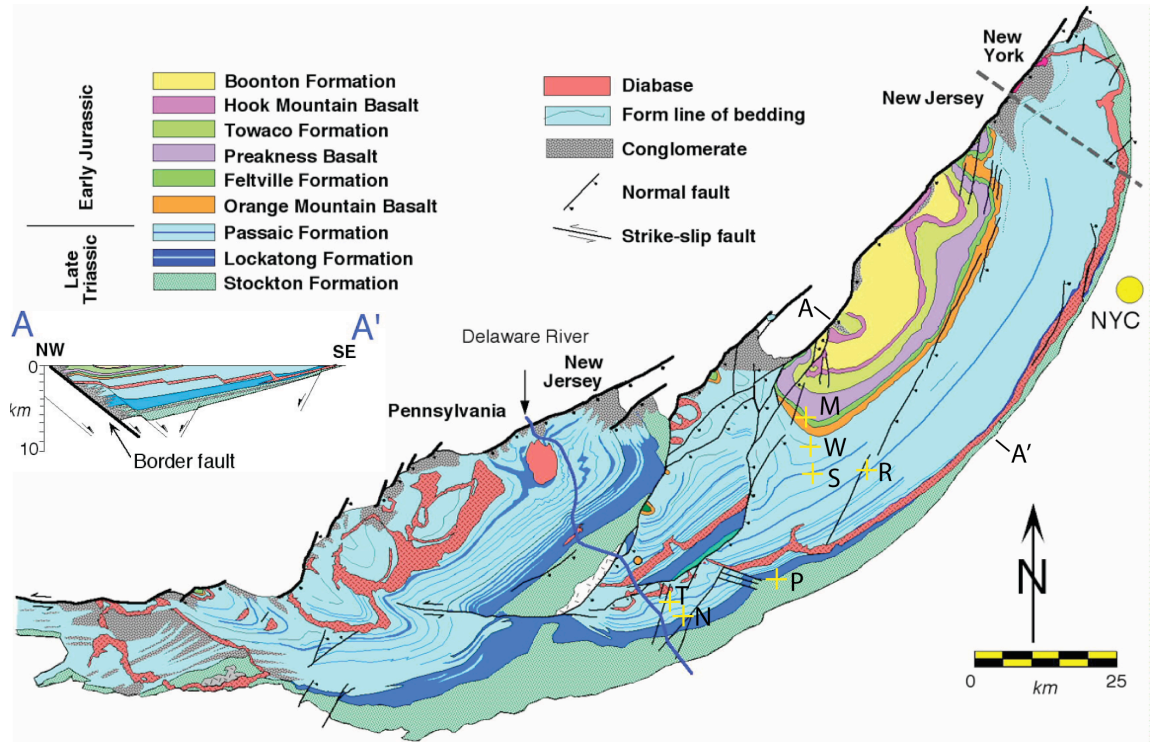


Figure 5.1: Map of the Newark basin (modified from Schlische (1992)) showing location of the Newark Basin Coring Project (NBCP) cores (yellow crosses), P = Princeton, N = Nursery, T = Titusville, R = Rutgers, S = Somerset, W = Weston Canal, M = Martinsville. Location of cross section from A to A' is denoted on the map and is perpendicular to the dip direction.

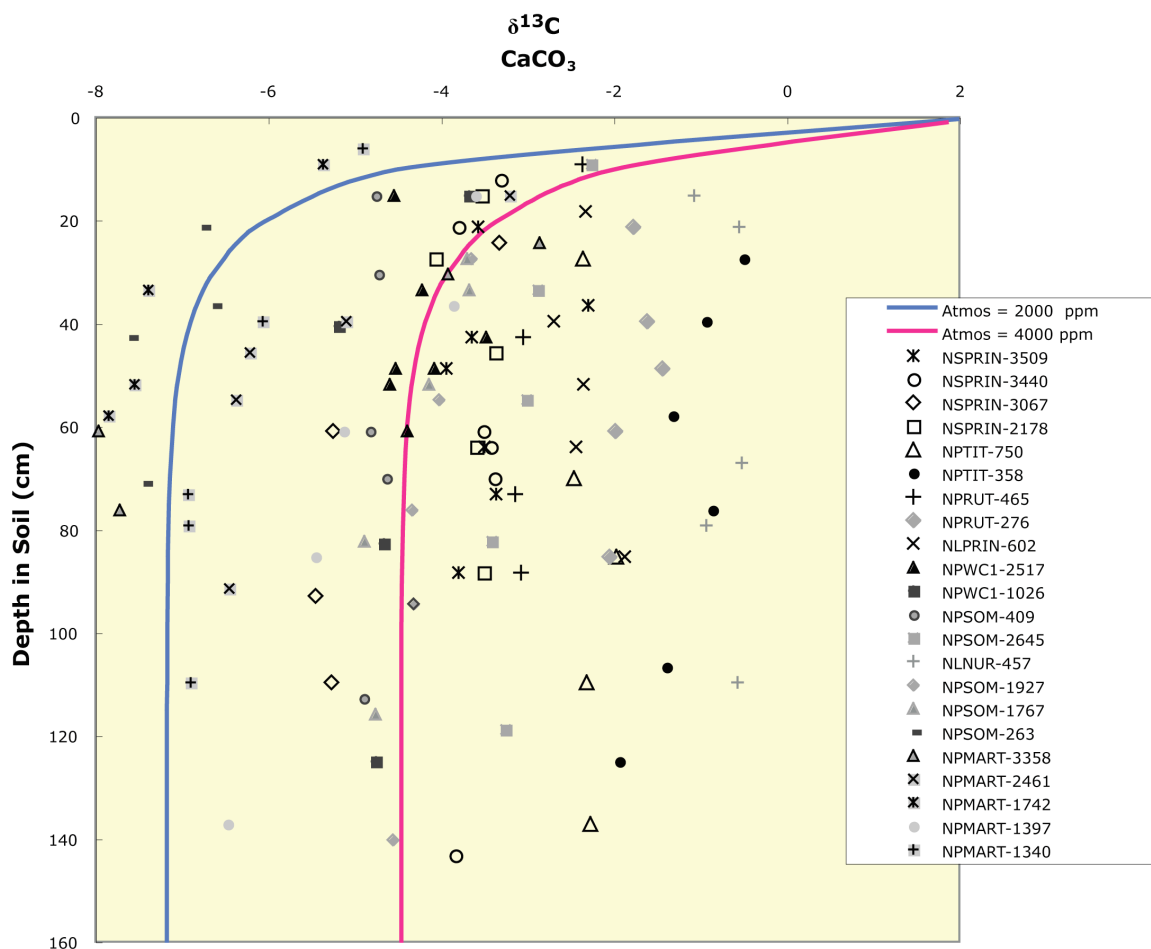


Figure 5.2: Down-profile $\delta^{13}\text{C}$ of pedogenic carbonates (δ_{cc}) from selected soils in the NBCP Newark basin composite section. Equilibrium down-profile means are used to calculate $p\text{CO}_2$. Observed δ_{cc} is compared to the δ_{cc} values predicted by the diffusion model at atmospheric CO_2 concentrations of 2000 ppm (blue line) and 4000 ppm (pink line) (after Quade et al., 1989). For this demonstration only, atmospheric $\delta^{13}\text{C}\text{CO}_2$ was set to -6.5‰ , soil $\delta^{13}\text{C}_{\text{org}}$ was set to -26.5 , with an exponential production function and characteristic depth of production at 15 cm (other parameters described in text). For all $p\text{CO}_2$ estimates made in this study, the $\delta^{13}\text{C}_{\text{org}}$ was measured directly and used as a model input. Soil carbonate above 20cm in the profile was rare; note that stabilization of measured δ_{cc} is commonly well below 50cm soil depth. Only the mean of the equilibrium δ_{cc} values were used to calculate $p\text{CO}_2$ in this study.

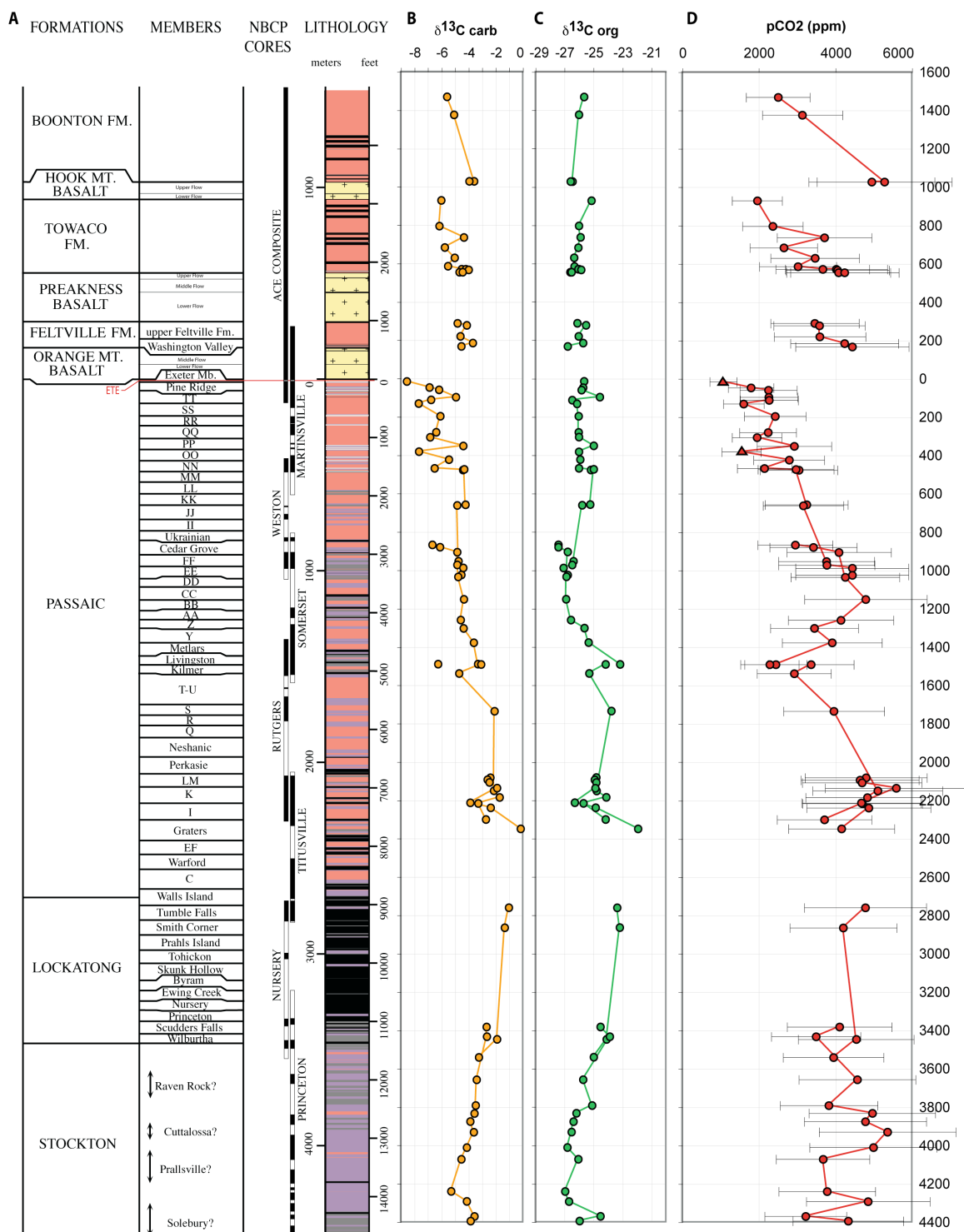


Figure 5.3: A. Newark basin formations and members, compared to the depth extent of each NBCP core and corresponding lithostratigraphy in composite section (Olsen et al., 1996a). Black (normal polarity) and white (reversed polarity) bars through the cores are magnetic polarity reversals from Kent et al., (1995) and Kent and Olsen (1999). ACE (Army Corps of Engineers) composite is based on a series of geotechnical cores that span the CAMP extrusive interval in high resolution (Fedosh and Smoot, 1988; Olsen et al.,

1996b; Schaller et al., 2011a). **B.** Equilibrium $\delta^{13}\text{C}$ of pedogenic carbonates from NBCP cores, data points connected by lines corresponding to individual cores. **C.** $\delta^{13}\text{C}$ of Organic Matter, lines connected as in B. **D.** pCO_2 calculated from B and C using Eqn. 1. Red points with error bars represent pCO_2 values at $S(z) = 3000 \pm 1000$ ppm. Triangles are samples from outcrop.

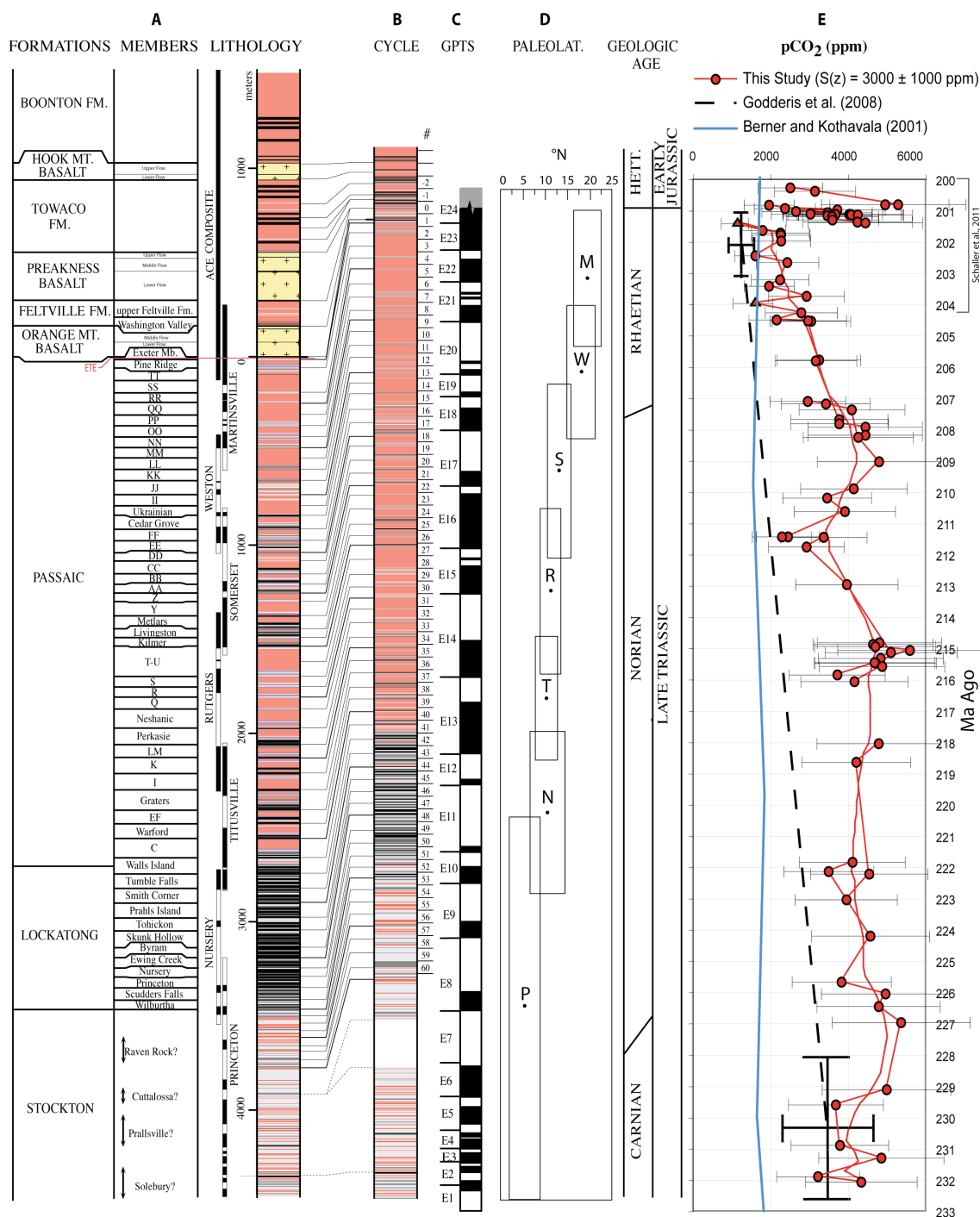


Figure 5.4: A. Newark basin lithostratigraphy. B. Cyclostratigraphy of Olsen et al. (Olsen and Kent, 1996) C. Geomagnetic polarity timescale of Kent and Olsen (1999) D.

NBCP core mean paleolatitudes from Kent and Tauxe (2005) corrected for inclination flattening. **E.** Calculated $p\text{CO}_2$ from this study (at $S(z) = 3000 \pm 1000$ ppm), compared to model output of GEOCARB III (Berner and Kothavala, 2001) (blue line) and Godderis et al. (2008) (black dashed line and points with error). Bracketed section of $p\text{CO}_2$ data is from Schaller et al. (2011a), triangles are samples from outcrop.

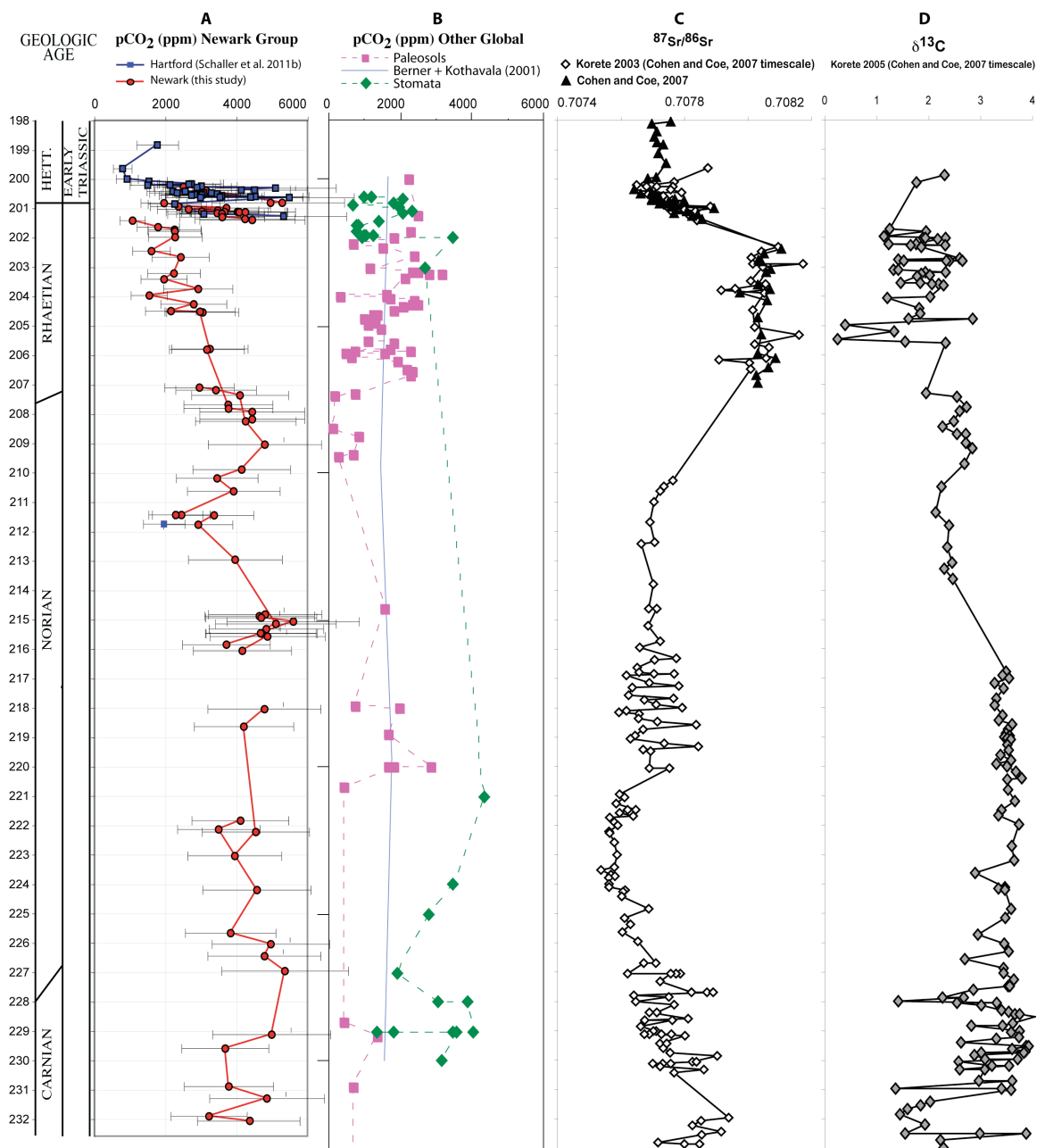


Figure 5.5: A. Newark NBCP composite $p\text{CO}_2$ from this study; $p\text{CO}_2$ from the Hartford basin from Schaller et al. (2011b). B. $p\text{CO}_2$ reconstructed from pedogenic carbonates from other sections (paleosol estimates from: Cleveland et al., 2008; Ekart et al., 1999; Royer et al., 2004). Stomata-based estimates are compiled from Retallack (2001), and McElwain et al. (1999) (using timescale of Kent and Clemmensen (1998)) C. Sr isotope record compiled from Tethyan sections by Korte et al. (2003), and from Cohen and Coe

(2007), plotted using the timescale of Cohen and Coe (2007). **D.** $\delta^{13}\text{C}$ of marine carbonates from Tethyan sections (Korte et al., 2005).

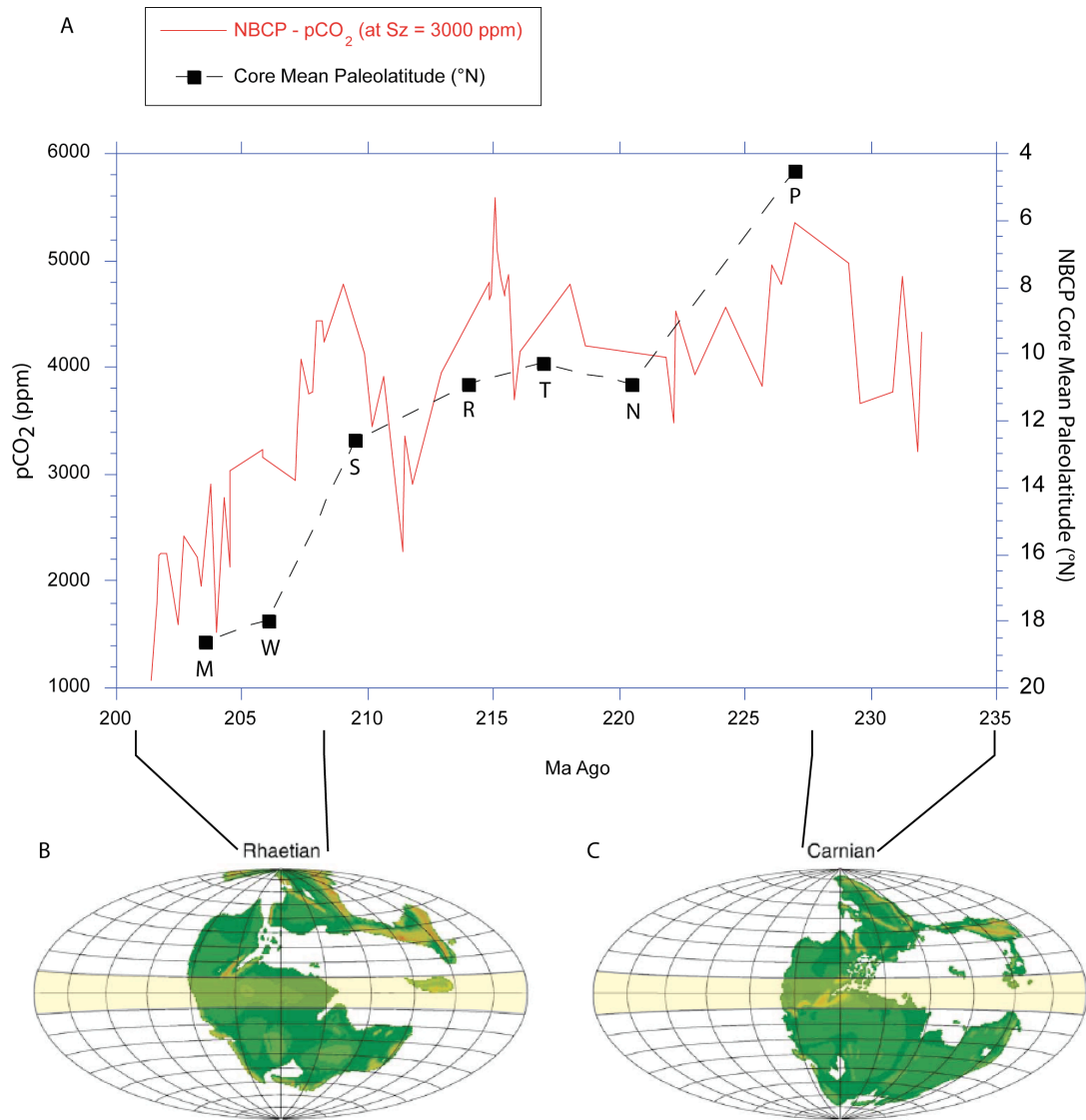


Figure 5.6: **A.** NBCP pCO₂ (at S(z) = 3000 ppm, red line), compared to NBCP core mean paleolatitudes (in °N) corrected for inclination flattening (Kent and Tauxe, 2005) (black boxes; P = Princeton, N = Nursery, T = Titusville, R = Rutgers, S = Somerset, W = Weston Canal, M = Martinsville). **B.** Rhaetian, and **C.** Carnian paleogeography from Godderis et al. (2008), based on reconstruction of Besse and Courtillot (2002). Highlighted region corresponds to the area between 10° N and 10° S latitude.

Chapter 6

Concluding Remarks and Future Directions

6.1. In brief

The evidence I present in Chapters 3 through 5 of this dissertation has revealed two fundamental aspects of Earth's carbon cycle:

1. The rapid eruption of a large igneous province (LIP) of comparable size to the Central Atlantic Magmatic Province can result in a transient perturbation of atmospheric $p\text{CO}_2$; and the longer-term consequence of rapidly emplacing such a huge quantity of basalt centered over the equatorial humid belt is an overall net decrease in $p\text{CO}_2$ due to the consumption of CO_2 by silicate weathering.
2. Continental weathering may be a more important forcing of long-term $p\text{CO}_2$ than changes in ocean crust production. When balanced against constant mid-ocean ridge degassing, the distribution of continental area constitutes a major sink-side forcing.

These two salient findings were the result of coordinated tests of well-formulated hypotheses, but the implications are best understood from a systems perspective as parts of a whole. In this concluding chapter I consider the overall findings of this dissertation in the context of Earth's long-term carbon cycle as if we had run a series of natural

experiments: first an experimental determination of long-term steady state (Chapter 5), which sets the stage for an experimental perturbation of the system (Chapters 3 and 4). As with any truly noteworthy suite of observations of the natural world, these findings generate a series of questions that remain outstanding, which are explored in more detail in the following sections, and represent points for future work.

6.2. Natural experimental equilibrium state

In essence, Chapter 5 of this work constitutes a test of the equilibrium conditions of Earth's carbon cycle in the Late Triassic. The goal was to test the hypothesis of Godderis et al. (2008), who propose that a 3-fold decrease in atmospheric $p\text{CO}_2$ through the Late Triassic was the result of the increase in continental area within the tropical humid belt that accompanied Pangea's northward migration. They use a carbon cycle mass balance model coupled to a general circulation model (GCM), with fixed degassing from the mid-ocean ridge complexes. The data presented in Chapter 5 tend to support this hypothesis, even when the details of the decrease in $p\text{CO}_2$ observed from the Newark basin are compared in detail to the record of Pangea's northward movement deduced from the mean paleolatitude of the NBCP cores.

Because changing the rate of ocean crust production changes the amount of CO_2 degassed from mid-ocean ridges, BLAG-based models (Berner et al., 1983) use an inverted sea level record to infer changes in mid-ocean ridge volume when establishing equilibrium. This record shows little trend in the Late Triassic, and consequently, BLAG models do not produce the ~3-fold decrease in $p\text{CO}_2$ through the interval. Although this finding does imply that changes in crustal production are probably not the primary driver

of long-term changes in $p\text{CO}_2$, we can say with much greater certainty that the increase in continental area within the tropical humid belt drove the massive late Triassic decrease in $p\text{CO}_2$.

Therefore, we've determined the late Triassic equilibrium state as a primary function of changes in the distribution of continental area changing the rate of silicate weathering, which is balanced against constant degassing from mid-ocean ridges. This steady state condition (more appropriately, a dynamic equilibrium, since $p\text{CO}_2$ is being drawn down) is an ideal and informative background state for the perturbation of the system that is the focus of chapters 3 and 4. However, it leaves a few open questions:

1. Is the distribution (and migration) of continental area a fundamental driver of the global carbon cycle through atmospheric $p\text{CO}_2$ in other periods of Earth history?
Answering this requires more tests of the long-term equilibrium state of the carbon system.
2. Can the BLAG hypothesis, where atmospheric $p\text{CO}_2$ is a primary function of ocean crust production, coexist as a module within a carbon cycle that is driven primarily by weathering, forced by changes in the distribution of continental area?
3. What explains the higher frequency variability in the Late Triassic $p\text{CO}_2$ record, are these smaller amplitude changes the result of changes in ocean crust production (as a module with a weathering forced system), dynamic rates of continental weathering, or forced by exchange of carbon with the organic reservoir?

These questions represent avenues of significant further work that will be addressed by future efforts. Against this backdrop, perturbations such as described in third and fourth chapters do give us insights into some of these questions. Here I elaborate only on those that I see as major holes in our understanding, with a heavy degree of speculation on their causes.

6.3. Natural experimental perturbation

In effect, Chapters 3 and 4 take advantage of a natural experiment to test the effects of a transient perturbation on the equilibrium set up through the Late Triassic. As discussed above, the overall driver of long-term $p\text{CO}_2$ change in the Late Triassic is the sink-side process of continental weathering. In the context of a weathering forced system, the eruption of the sizable Central Atlantic Magmatic Province (CAMP) represents a significant potential CO_2 source- and sink-side perturbation. The detailed $p\text{CO}_2$ data presented in Chapter 3 demonstrates that there was indeed a transient $p\text{CO}_2$ increase perturbing the Late Triassic equilibrium state, and Chapter 4 illustrates that the long-term result of emplacement of the CAMP was a net decrease in $p\text{CO}_2$ due to weathering. The broader implications of these findings, as they help us understand the fundamental controls on Earth's carbon cycle, and questions that remain open are discussed below.

6.3.1. Short-term perturbation

The $p\text{CO}_2$ estimates presented in Chapter 3 (Schaller et al., 2011a) show a consistent $\sim 2000 \pm 700$ ppm pre-eruptive background, with an increase to $\sim 4400 \pm 1200$ ppm above the first eruptive unit, followed by a ~ 200 kyr decrease to near pre-eruptive

concentrations. This pattern is repeated more or less above each basaltic unit (see Fig. 3.1 for details). Among the findings already iterated in that chapter, there are some broader implications that highlight fundamental traits of Earth's carbon cycle.

The first major finding is that the long-term carbon cycle could indeed be perturbed by the eruption of the LIP. If the CAMP lavas were rapidly extruded, and resulted in such a dramatic atmospheric $p\text{CO}_2$ effect, we may expect other massive continental LIP's to have a similar effect. The potential for such a response (both short and long term) will be explored in more detail in the next section, but certainly voluminous LIPs such as the Siberian traps (Coffin and Eldholm, 1993) have the potential to perturb the atmospheric reservoir. So far, stratigraphic uncertainty and the lack of appropriate lithologies sequencing the extrusives make testing this difficult. However, more fundamentally, an outstanding question still remains as to how the atmospheric perturbation due to a LIP is actually accomplished.

In the Supplement to Chapter 3, we reply to a comment by Rampino and Caldeira (2011), who note that a modeled 20-kyr release of $\sim 1.2 \times 10^{16}$ kg (2.5×10^{17} moles) of CO_2 only produces ~ 400 ppm atmospheric perturbation. This release is about what can be derived from the projected volume of extrusives corresponding to the Orange Mountain Basalt (OMB) and its eruptive equivalents (McHone, 2003). However, we observe roughly a doubling of $p\text{CO}_2$ from ~ 2000 ppm to ~ 4000 ppm, with a time constraint to within a precession cycle. We therefore argue that the extrusion of the first pulse of volcanism probably occurred over a timescale of less than 1000 years (the timescale of ocean overturning and rapid CO_2 absorption), which would produce roughly the atmospheric signal we observe (Schaller et al., 2011b).

Paradoxically, models using a release time sufficiently longer than 1000 years (e.g., 10 kyr) require nearly 10-times more carbon to produce results that match the increase observed in the Newark basin. Thus, a glaring implication is that the timescale of the eruption makes a prediction about the source of the CO₂ degassed in association with the volcanic activity: If an extremely rapid eruption, then a smaller amount is necessary and the CO₂ could be mostly volcanogenic, but if the eruption time was longer than ~1000 years, another reservoir must be tapped.

It has been suggested that a LIP may induce massive thermal degassing of CO₂ from sediments rich in organic carbon, or liberate large quantities of methane from clathrates (Svensen et al., 2007; Svensen et al., 2004; Svensen et al., 2009a; Svensen et al., 2009b). These possibilities cannot be excluded, but as discussed in Chapter 3S, are not supported by our organic carbon isotope record, and therefore require more detailed data to address. Notably, others have reported a carbon isotope excursion that is associated with the Triassic-Jurassic transition strata in marine sections (e.g., Hesselbo et al., 2002; Ruhl et al., 2011), but the exact relationship of these to the continental section is not clear (Whiteside et al., 2010). Alternatively, recent geochemical work indicates that much more CO₂ may be contained in flood basalts than previously thought (Sobolev et al., 2011), which substantially increases the estimated effusive flux potential of a given volume of basalt.

A perhaps under-appreciated implication of these data is that a massive input perturbation of the atmospheric reservoir appears to have had a very short, and overall relatively minor effect on the carbon cycle (see Fig. 5.6, for perspective). The huge CO₂ release due to the CAMP probably caused a transient warming and attendant

environmental changes, but these effects were effectively neutralized within a few hundred thousand years as $p\text{CO}_2$ returned to pre-eruptive concentrations. Only when looking at the long-term effects of emplacing 10^7 km^3 of basalt centered over the equatorial humid belt do we begin to appreciate the lasting effects a LIP may have on the carbon cycle. However, the weathering effects of a particular LIP are not uniformly attributable to all LIPs or continental flood basalts; as discussed in section 6.3.3, these processes are highly dependent on the location of the extrusives in relation to the zones of most active weathering at Earth's surface.

6.3.2. Are these $p\text{CO}_2$ pulses present in other basins?

An obvious next step is to check for the location of these $p\text{CO}_2$ pulses in the other basins (e.g., the Culpeper basin to the south of the Newark basin, and the Fundy basin, north of the Hartford basin), a worthwhile pursuit that would answer two main questions. First, are these $p\text{CO}_2$ pulses something local to the basalts themselves, and not, in fact a function of atmospheric $p\text{CO}_2$? Experimentally, all that's necessary is to locate these pulses in sequence, in high-resolution sedimentary strata that are devoid of CAMP basalts, but are known to be stratigraphically equivalent to basalt-bearing strata. A hint that the CO_2 pulses are not related to local effects of the basalts is indicated by the striking correspondence between the Hartford and Newark basin records (Fig. 4.4), particularly where a fourth increase in $p\text{CO}_2$ is noted above the final basalt, which we attribute to a magmatic event for which we have no local extrusive evidence. These observations are of course subject to alternate interpretations. However, for example, identification of the $p\text{CO}_2$ peaks associated with the Orange Mountain and Preakness Basalts and their magmatic equivalents, in the small Deerfield basin, where only a

Preakness-equivalent basalt is present (see Whiteside et al. (2007) for review), would be convincing evidence that the pulses were global.

The second objective of locating these pCO₂ pulses in other basins is to take advantage of their stratigraphic usefulness. Since atmospheric CO₂ is homogenous on a rapid timescale, its concentration should be recorded contemporaneously at disparate global sections. If the four individual pCO₂ pulses noted in the Newark-Hartford section are indeed related to individual magmatic events, and not local manifestations, then finding them in ordered sequence, corresponding to basaltic units in e.g. the Argana or Central High Atlas basins would demonstrate that the basalts were temporally related to one another. A challenge to these pursuits is that high temporal resolution (≥ 100 kyr) is needed to capture the transient pulses of CO₂, so reliance on sequences of poorly developed soils may thwart these efforts.

In fact, the Newark and Hartford basins are probably ideally situated to capture the transient effects associated with individual extrusive units of the CAMP because only the largest events/flows reach the relatively distal location of these basins. As discussed above, only very large and rapid eruptions are likely to produce a measurable CO₂ pulse (if the CO₂ is basalt derived), and more protracted eruption rates, or plentiful, smaller eruptions over an e.g., 10-kyr timescale may not impart any effect on atmospheric pCO₂. Thus, those basins on the periphery of the proposed CAMP eruptive center (e.g., Wilson, 1997), such as the ENA basins, probably only show lithologic evidence of the largest eruptions (three flow-units, in the case of the Hartford and Newark basins). Therefore, these basins uniformly see pCO₂ changes that correspond to the largest eruptions, and since these locations have evidence of only the largest magmatic events, the pCO₂ pulses

correspond to basaltic units unambiguously. On the other hand, the Central High Atlas basin may be geographically close to the center of the eruptive complex, and therefore preserve more eruptive ‘noise,’ while still recording the $p\text{CO}_2$ changes only associated with the largest events, even though the extrusive evidence of those events may be indistinguishable from the much smaller eruptions in those locations. In this way, the local thickness (or indeed, presence) of basalts in a particular location is not necessarily relevant to the environmental effects of the magmatic events, but the global $p\text{CO}_2$ pulses are effective at distinguishing signal to noise locally.

Finally, an obvious outstanding issue is the relationship between the end-Triassic extinction (ETE) and the eruption of the CAMP. Because LIPs are often temporally associated with mass extinctions (e.g., see Wignall, 2001), and the ETE is located just below the first evidence of the CAMP eruptions in the ENA basins, this is a point of much interest and speculation. Section 6.4 of this chapter is devoted to discussing these issues.

These natural, short-term perturbations of the Late Triassic carbon cycle show that the perturbing forces must be rapid and severe, but that they are also transient and nearly neutralized in a few hundred thousand years. Chapter 4 looks at the long-term implications of these perturbations, effects that are specifically due to the basalts, and may be the only long-lasting effects of a LIP eruption on Earth’s carbon cycle. The implications of those observations are discussed below.

6.3.3. *Basalt weathering triggers*

The $p\text{CO}_2$ data from the Hartford basin presented in Chapter 4 confirms findings in the Newark, and demonstrates that the long-term effect of a Large Igneous Province may indeed be a net-decrease in $p\text{CO}_2$ below the pre-eruptive concentration. This finding has significant implications for long-term regulation of Earth's climate, and makes the prediction that a similar LIP, erupted as rapidly into the tropical humid zone, may have a similar long-term effect on atmospheric $p\text{CO}_2$. Conversely, a continental flood basalt rapidly erupted into an arid belt may have no immediate (10^6 -year) sink-side effect on Earth's carbon cycle (e.g., see Kent and Muttoni, 2008), and only immediately perturb the atmospheric reservoir with a massive potential input. While Chapter 3 represents a very significant finding regarding the short-term environmental effects of a LIP, the data presented in Chapter 4 imply that the geographic distribution of these extrusive events can have differential effects on Earth's long-term climate.

For clarity's sake, the working hypothesis that has emerged from these observations is that similar massive and rapidly erupted equatorial continental flood basalts could result in a net drawdown of $p\text{CO}_2$. While it is interesting to speculate on the unique potential for long-term sink-side impact of other LIPs throughout Earth history, an experimental approach is of greater value; finding a massive and rapidly erupted equatorial continental flood basalt that did not result in a drawdown of $p\text{CO}_2$ would most efficiently cast doubt on my hypothesis.

With that in mind, I make the case here that the Emeishan LIP is an excellent candidate to test this hypothesis. The Emeishan province was extruded in the late Permian on the South China cratonic block (Ali et al., 2005; Courtillot et al., 1999),

which was situated effectively equatorially at the time (Kent et al., 1987; Opdyke et al., 1986). The observations of Schaller et al. (2011c) predict that a decrease in atmospheric $p\text{CO}_2$ should follow the eruption of this LIP if it was rapidly extruded (<100 kyr?) and remained exposed in the equatorial humid belt. If it was not extremely rapidly extruded, the basalts themselves may not result in a $p\text{CO}_2$ pulse (Schaller et al., 2011b), but if emplaced in sufficient quantities, remain a reactive core of continental material that is likely to be ~ 10 -times more weatherable than the crust it overlays (Gaillardet et al., 1999).

Appropriate paleosols are preserved in continuous Late Permian continental sequences in Europe (Inozemtsev and Targulian, 2010), Antarctica (Krull and Retallack, 2000), and perhaps even South China (He et al., 2003; He et al., 2010). These soils could be used to identify any potential transient $p\text{CO}_2$ drawdown, and if high enough continuous resolution (or superposition with Emeishan basalts) is available, may be employed to test the possibility of a short-term $p\text{CO}_2$ perturbation immediately after eruption. Unlike attempts to capture the increase in $p\text{CO}_2$ immediately following a LIP eruption (such as that of the CAMP), the transient decrease occurs over the million-year scale, and has a much higher probability of being detected from afar (although excellent chronostratigraphy is needed to ascribe changes to the basalts themselves).

If erupted rapidly, it seems apparent that continental flood basalts may lead to transient perturbations of the global carbon cycle on both the source and sink sides, but what about submarine LIPs? In the case of a submarine flood basalt, the effusive potential per unit of erupted volume may be comparable, and hence, a transient perturbation of atmospheric $p\text{CO}_2$ may be expected if the extrusion was rapid enough.

However, the accelerated long-term decrease in $p\text{CO}_2$ due to consumption of CO_2 by hydrolysis of the basalts may not occur, simply because the basalts themselves are removed from the active weathering zones (since no significant chemical weathering occurs under water (Alt and Teagle, 1999; Berner, 1991)). Therefore, we expect rapidly erupted oceanic LIPs to produce a transient source-side perturbation, but probably have no sink-side effects. Similarly, if a flood basalt of comparable volume to the CAMP were to erupt in the modern Sahara desert, we would expect very little long-term future weathering of that province (and hence, no $p\text{CO}_2$ decrease) until the basalts were tectonically relocated into the humid belts where chemical weathering is most active. Therefore, LIPs themselves represent highly reactive masses distributed across Earth's surface that can be brought into play at any time during their exposed (or exhumed) history by tectonic reorganization (e.g., Kent and Muttoni, 2008).

In summary, we have learned two essential things from the atmospheric $p\text{CO}_2$ response to the CAMP that can guide predictions about the numerous other LIPs throughout Earth history: 1. The size and rapidity of the eruptions are most likely the dominant control on the potential for a short-term $p\text{CO}_2$ increase; 2. The location of the erupted basalts at the time of extrusion (subaerial in the humid belts vs. arid zones or submarine) predicts the immediate million-year scale effects of the LIP. Relocation of the basalts while their surfaces remain exposed makes these provinces essentially “potential CO_2 sponges” that may be tectonically redistributed through space and time, such that their $p\text{CO}_2$ -reducing effects could be felt from 10^5 to 10^7 years (or longer) after their extrusion. Thus, over the long-term, LIPs may be more important to the evolution of Earth's climate as net sinks for CO_2 , rather than as net sources. These processes are all

independent of the long-term source-side degassing of CO₂ from ocean crust production, but have drastic implications for the sink-side processes that apparently maintain equitable climates on Earth's surface.

6.4. Implications regarding the End-Triassic Extinction

An outstanding question remains concerning atmospheric pCO₂ at the time of the End Triassic Extinction events (ETE). The data from Chapter 3 of this dissertation (Schaller et al., 2011a) indicate that the increase in pCO₂ due to eruption of the first pulse of the CAMP was the first detectable increase in the vicinity of the extinction events. However, the temporal sequence of events is incorrect to demonstrate a causative relationship to the extinction events: pre-CAMP background pCO₂ is roughly ~1500 ppm about 1.5 m (~1000 kyr) below the ETE strata in the Jacksonwald section of the Newark basin, followed by ~13 m of sediment to the base of the Orange Mountain Basalt (see Fig. 6.1). No pCO₂ estimates have so far been possible in this 13 m section (from the Exeter Township Member) because of poor exposure and diagenesis of the post ETE strata. However, this section contains one of the best expressions of the ETE fern spike (and iridium anomaly) in the eastern North American basins (Fowell et al., 1994; Fowell and Traverse, 1995; see review in Olsen et al., 2002). Such a glaring lack of data provides significant impetus for a small-scale drilling initiative to recover this interval at the Jacksonwald syncline, near Exeter PA. A definitive estimate of pCO₂ directly related to the extinction events is possible only if the interval from below the ETE to the base of the Orange Mountain Basalt contains appropriate paleosols.

Corollary sections from elsewhere in the Newark basin provide preliminary pCO₂ estimates that may fall stratigraphically above the ETE, and also show elevated atmospheric CO₂ concentrations (e.g. ACE core C-87, ~100 km from the Exeter Twp. Member, Fig. 6.1), but the lack of affirmative extinction strata makes these connections tenuous. Data from ACE core C-87 is provided in Figure 6.1, where 3 overlapping paleosols yield depth-equilibrated $\delta^{13}\text{C}$ of pedogenic carbonate around $\sim -5.7\text{‰}$ and organic $\delta^{13}\text{C}$ around ~ -27.1 , which yield pCO₂ estimates of $\sim 3300 \pm 1100$ ppm. In lieu of drilling the ETE section at Jaksonwald, a comprehensive analysis for the location of the ETE strata in ACE core C-87 is essential. However, even these existing pCO₂ estimates are insufficient to demonstrate arguable causality if the ETE-event level isolated as drawn in Figure 6.1.

6.5. References

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6.6. Figures and Captions

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