The biogeochemical consequences of the mid-Cretaceous superplume

A. Hope Jahren*
Department of Earth, Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA

Abstract
Superplumes have been put forward as a driving mechanism for a variety of global phenomena, ranging from geomagnetic reversal anomalies to global climate warming via massive additions of volcanic CO₂. Here I propose that rates of uplift caused by modern superplumes would result in the liberation of hundreds of Gt of carbon from methane clathrates on a timescale from tens to hundreds of millions of years. The associated eruption of the Ontong-Java flood basalts would additionally destabilize hundreds of Gt of carbon from methane hydrates during the Aptian-Albian. Evidence of this methane release is recorded in the early Aptian (ca. 117 Ma) carbon isotope records of marine carbonate, marine organic carbon, and terrestrially photosynthesized carbon as a 3–5% negative excursion. As this methane release was oxidized within the biosphere, it would have resulted in massive chemical cycling disruption within the ocean and on land, including widespread oceanic anoxia, and the out-competition of conifers by angiosperms at mid- and high-latitudes. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction: a superplume in the mid-Cretaceous

Although J. Tuzo Wilson is credited with the original suggestion of mantle plumes (Wilson, 1966), conceptualizing them as rising hot jets of mantle material, the first suggestion of a “superplume” was the description of an active plume head spanning 2000 km (White and McKenzie, 1989). A ~40 Ma period of increased spreading rate and basaltic magma generation is recorded in the geologic record beginning at 120 Ma; taken in context with production-rate estimates during the last 150 million years, a 50–75% increase in new oceanic crust production was determined for the LNS (“Long Normal Superchron”) of the Cretaceous. This dramatic increase was attributed to a superplume rising beneath the Pacific Ocean with minimum dimensions 6000 by 10,000 km (Larson, 1991b), known as the “mid-Cretaceous (~125 Ma) superplume.”
The methods of reasoning used to define the mid-Cretaceous superplume have met with some criticism; it has been suggested that using the continental stratigraphic record of sea-level change and the ridge volume hypothesis of eustasy is a better approach for estimating the igneous production rates (Gaffin, 1992). Large discrepancies were found when estimates of eustatic sea level change resulting from the plume were compared with generally accepted values, leading the authors to suggest that the rate of seafloor and plateau creation (and thus the size of the mid-Cretaceous plume) had been overestimated using Larson’s (1991b) methods (Hardebeck and Anderson, 1996).

However, theoretical work supports the idea that a superplume originating at the core-mantle boundary could have led to an increase in ridge and plateau basalt production. The mechanism suggested is that cold subducted material triggers catastrophic convective overturn within the mantle, leading to superplume formation (Honda et al., 1993; Weinstein, 1993). A superplume impinging on the surface beneath a mid-ocean ridge would lead to an increase in ridge-push forces and spreading rates (Bott, 1993). In addition, the increase in below-surface temperatures due to the presence of the superplume could increase crustal production (McKenzie and Bickle, 1988). The assumption that crust production at mid-ocean ridges can be taken as a measure of deep-seated mantle convection has also been questioned; specifically, concurrent subduction has been suggested as a potential controller of spreading rates, and confirmation by geochemical measurements has been called for to fortify the crust-production/superplume link (Cox, 1991). Towards this end, Nb/Y vs. Nb/Zr characteristics of basalt lavas from the Shatsky Rise, the Ontong Java Plateau, and Sakhalin Island of the South Pacific indicated similarity to Polynesian lavas formed by upwelling of a deep mantle superplume (Tatsumi et al., 1998: Fig. 2). The Ontong Java Plateau was dated as originating between 120 and 90 Ma using Ar–Ar methods (Tejada et al., 1996), indicating that the South Pacific superplume was active in the mid-Cretaceous.

Geophysical models have predicted that low-density mantle material (such as a superplume) positioned under an oceanic ridge would result in uplift that would more than double pre-existing compressional stresses in neighboring plate interiors (Bott, 1993). Evidence of short-lived pulses of mid-Cretaceous (early Aptian to late Albian) deformation, metamorphism, uplift, and hiatus sedimentation is widespread in terranes bordering the Cretaceous Pacific Ocean, leading to the suggestion that mantle processes associated with the mid-Cretaceous superplume indirectly produced widespread deformation on what was then the Pacific margin. Examination of 22 such terranes showed that there was widespread guyot emergence in the early Aptian (Vaughan, 1995), marking the beginning of the mid-Cretaceous increase in spreading rates (Larson, 1991b). Specific to the Colombian record discussed below, an hiatus in sedimentation during the mid Aptian throughout western South America has been documented (Marcellari, 1988), perhaps indicative of uplift; metamorphism and deformation specific to the Aptian are widespread in Jurassic and lower Cretaceous rocks extending from Colombia to Mexico (Freydier et al., 1997). All of these lines of evidence are suggested to reflect superplume activity during the Cretaceous.

A variety of global phenomena have been explored as resulting from the mid-Cretaceous superplume; for example, it has been suggested that superplumes trigger geomagnetic reversal anomalies based on observations from the mid-Cretaceous (Larson and Olson, 1991). The associated outburst of oceanic crust production has been linked to global climate warming by more than one researcher via massive additions of volcanic CO₂ and associated effects on biogeo-
chemical cycling (Caldeira and Rampino, 1991; Larson, 1991a). Here I suggest that the mid-Cretaceous superplume dramatically affected global biogeochemistry through the massive dissociation of methane hydrates and resultant oxidation within the ocean and the atmosphere.

2. Methane hydrates

Methane hydrates are solids composed of water molecules encasing molecules of methane; they are formed mainly by the metabolism of organic carbon by chemoheterotrophs in marine sediments. Many gases (e.g. ethane, propane, carbon dioxide) are found in gas hydrates, but methane is thought to be the most common naturally-occurring type (Kvenvolden and McMenamin, 1980). Methane hydrates are physically stable across temperature conditions of −8 to +14 °C and pressure conditions corresponding to an ocean depths of 200 to >6000 m (with slight dependence on pore-water composition (Dickens and Quinby-Hunt, 1994, 1997)), making them abundant in permafrost regions and on the outer continental margins (Katz et al., 1959; Kvenvolden and Lorenson, 2000). BSR (bottom-simulating reflector) data from globally-distributed oceanic sites indicates that the present-day amount of methane hydrate carbon contained in continental margins can be conservatively estimated as 10,000 Gt (1 Gt = 10¹⁵ g) (Kvenvolden, 1988). This value is large compared to all terrestrial carbon reservoirs, and is ~20 times greater than the amount of carbon presently stored in living terrestrial biomass (Sundquist, 1993). The amount of carbon stored as methane hydrate is huge compared to present-day carbon storage in the Earth’s atmosphere (600 Gt) and to carbon in ocean surface waters (630 Gt) (Holland, 1961). Methane hydrates can be destabilized by small increases in temperature or decreases in pressure, leading to methane gas liberation and ultimately, methane addition to the ocean and to the atmosphere.

The geographic expanse of large areas with geophysical and geochemical conditions favorable to methane hydrate stability was highlighted by a study of the European continental margins that indicated that the entire western continental margin of Europe is conducive to hydrate formation (Miles, 1995). The total potential volume of gas hydrate stored in the global sedimentary reservoir has the potential to change considerably over geologic time because the earth’s changing environments affect both the potential for biological production and geological storage; however, no agreement exists regarding how much change has occurred or in what direction. It has been claimed that total carbon stored in methane hydrate has likely increased since the Triassic due to increases in total continental margin length and a decrease in bottom water temperature (Dickens, 2001). However, it has also been suggested that the concentrations and areal extent of Phanerzoic methane hydrate was significantly greater than in modern sediments due to increased nutrient availability in ancient oceans and sluggish circulation patterns that favored the biological production of methane (Bratton, 1999).

3. Recognizing methane release in the terrestrial geochemical record

Massive dissociation of methane hydrates over time periods as short as 10⁴ years have been suggested at the Latest Paleocene Thermal Maximum (LPTM, 55.6 Ma) (Dickens et al., 1997)
bringing with it widespread climatic disruption. The unusually low carbon stable isotope composition of methane clathrates ($\delta^{13}C–CH_4$ ranges from $-57$ to $69\%$ off the coast of northern California: Valentine et al., 2001) suggests that hydrate dissociation should be geochemically conspicuous in paleoclimate records. The average $^{13}C$-signature of methane hydrate ($\delta^{13}C\approx-60\%$) (Kvenvolden, 1993) has been widely used to construct isotopic-mixing scenarios in which carbon from methane is incorporated into marine carbonate and terrestrial photosynthetic biomass. The LPTM (55.6 Ma) methane release was inferred at the from a negative $\delta^{13}C$ excursion ($\Delta = -2.5\%$) in the marine carbonate record (Dickens et al., 1995, 1997), as solubilized methane was incorporated into the oceanic food-web. These records had been previously correlated to negative excursions of similar magnitude in the terrestrial record: soil carbonate $\delta^{13}C$ (Koch et al., 1992) and terrestrial organic matter $\delta^{13}C$ (Stott et al., 1996). Global biogeochemical response to such an event is thought to be extremely rapid (Norris and Rohl, 1999), and the brief interval at the LPTM is characterized by extensive climate disruption. Examples of such disruption include a rapid 4–8 $^\circ$C increase in deep-ocean, high-latitude and continental temperatures (Fricke et al., 1998; Kennet and Stott, 1991; Zachos et al., 1993); the fossil record also exhibits major turnovers in terrestrial and marine flora and fauna at this time (Aubry, 1998; Hooker, 1996; Thomas and Shackleton, 1996).

We recently reported on the carbon isotope composition of organic material from estuarine and near-shore terrestrial sediments of early Cretaceous age at three localities in the Cordillera Oriental of the Colombian Andes, South America (Jahren et al., 2001). Formations sampled span the majority of the early Cretaceous and were age-dated based on biostratigraphic correlation with well-established dinoflagellate and ammonite zones (Guerrero and Sarmiento, 1996). This sequence represents an $\sim18$ Ma interval with no evidence of depositional disconformity. Fig. 1b shows that carbon isotope values increase in the late Barremian ($\delta^{13}C\approx21\%$), followed by a dramatic decrease to $\approx-28\%$ in the early Aptian, which is followed by a sharp increase to $\approx-21\%$ in the mid-Aptian. There is no evidence for depositional discontinuities in this part of the section, and the samples representative of the dramatic excursion comprise $\sim100$ m of sediment (application of average sedimentation rates for the Fômeque formation suggest that this event was $<1$ Ma in duration). A comparison of these results to several published marine records (Fig. 1a) reveals similar trends in both records, but lower response magnitude in the marine record. Most notable is the much less dramatic, but apparent, negative excursion and positive return indicated in the marine record during the middle to late Aptian. This difference is explained by the 6.5:1 mass-ratio difference between carbon in the intermediate and surface ocean and the carbon in the atmosphere (Siegenthaler and Sarmiento, 1993), which results from a carbon isotope dilution mechanism between the $\delta^{13}C$ value of CO$_2$ in the atmosphere and the $\delta^{13}C$ value of dissolved carbon species in marine water. Thus over geologically short intervals, marine biotic carbon isotope signatures are less sensitive to changes in the $\delta^{13}C$ value of atmospheric CO$_2$ than those of vascular land plants, which fix atmospheric CO$_2$ directly.

Reconstruction of $\delta^{13}C$ changes in the atmosphere was performed using the average $\delta^{13}C$ values of strata within terrestrial sediments, including isolated cuticle and vitrinite, components unique to land plants. For C3 plants, which dominated Cretaceous ecosystems (Bocherens et al., 1993), isotopic fractionation during carbon assimilation is influenced by the discrimination due to differential diffusion of $^{12}CO_2$ versus $^{13}CO_2$ in air. This discrimination is imparted by the primary carbon fixation enzyme and ecophysiological factors that balance carbon gain with water loss in
Fig. 1. $\delta^{13}$C data from the Cretaceous: terrestrial and marine organic carbon (1b) and marine carbonate (1a) analyses. Overall time-scale (Harland et al., 1989), cross-correlates marine and terrestrial records to $\leqslant 1$ Ma. Key events (1c) (Coffin and Eldholm, 1993; Larson, 1991b; Marcellari, 1988; Sliter, 1989; Vaughan, 1995) of the early Cretaceous are included for comparison.
the leaf (Farquhar et al., 1989); reviewed in (Arens et al., 2000). In an analysis of a large data set (519 published δ¹³C plant measurements on 176 C₃ species). The relationship between the δ¹³C value of plant tissue and atmospheric CO₂ is linear and significant (r² = 0.91 for the full data set), allowing for an empirically-derived relationship [δ¹³C_{atmosphere} = (δ¹³C_{plant} + 18.67)/ 1.10] that could be used to estimate δ¹³C of atmospheric CO₂ from preserved terrestrial plant material (Arens et al., 2000). In actualistic tests to verify the predictive ability of this method, the relationship predicted both ancient and modern atmospheric δ¹³C values within the defined confidence interval in most mesic environments (Arens et al., 2000).

In addition, this finding has been confirmed through the analysis of modern accumulating sediments from several sites, all of which yielded an atmospheric prediction within 1.0‰ of the true modern value (Cabena, 1999). By using these methods, a negative excursion of ≈−5‰ was inferred in atmospheric CO₂ δ¹³C in the early Aptian, followed by a rapid positive compensation during the mid-Aptian, suggesting substantial disruption in global carbon cycling (Jahren et al., 2001). Of course any addition of isotopically light carbon to the atmosphere could drive such an excursion, including magmatically derived CO₂, volatilized organic carbon from standing or buried biomass, and methane. The rapid return to pre-excursion values can be explained by geo-logically rapid equilibration between the ocean and the atmosphere, as the composition of the atmosphere is “reset” by the overwhelmingly large reservoir contained in the intermediate and surface ocean. Based on the assumption that Cretaceous pCO₂ was about four times present-day partial pressure (≈2400 Gt of C) (Berner, 1990), simple source-mixing analysis estimates the amount of carbon (n) required from each of the potential sources to drive the negative atmospheric excursion: (2400 + n Gt C)* (δ¹³C_{atmosphere} early Aptian) = 2400 Gt C* (δ¹³C_{atmosphere} late Barremian) + n Gt C* (δ¹³C_{emission}). These calculations permit the rejection of the above reservoirs, including magmatically derived CO₂, as the source of ¹³C-depleted CO₂ because of the untenably large amounts that would be required to drive such a dramatic excursion (Table 1 and Jahren et al., 2001). Alternatively, only ~225 Gt of carbon from methane hydrates, = ~2% of the present-day oceanic reservoir, would have to be liberated in order to account for the excursion.

4. Methane release as the result of superplume upwelling

Methane hydrate stability in sediment pore spaces depends on temperature and pressure; processes as diverse as gradual pressure change due to sedimentary burial, submarine slope failure, lowering of sea-level, or increase in bottom water temperatures could liberate CH₄ (Kvenvolden, 1993). In addition, it is clear that a superplume’s activity affects the stability and movement of the earth’s crust: presently, there are several uplifted areas of the Earth’s surface that are thought to be associated with large-scale mantle upwelling. These areas are located in the south Pacific (McNutt, 1998) and near southern Africa (Gurnis et al., 2000; Lithgow-Bertelloni and Silver, 1998) and have several similarities to the mid-Cretaceous superplume. Both Larson (1991b) and McNutt (1998) have suggested that these superswells could be the nearly exhausted remnants of superplumes. Present-day superswell regions are typically thousands of km in diameter, are underlain by low-velocity material, and are uplifted at least 500 m (McNutt, 1998).

Uplift caused by superplume upwelling could have provided the physical disturbance necessary to liberate enough methane from methane hydrates to account for the isotopic excursion descri-
bed in the marine and terrestrial records. Fig. 2 depicts the reservoir of methane hydrate carbon subject to liberation as the result of uplift. Presently, conditions appropriate to methane hydrate stability comprise 30% of the oceanic seafloor (= ~1×10^8 km^2) (Bratton, 1999: Fig. 1). Using the global average of methane hydrate thickness = ~600 m specified by Bratton (1999), the hydrate-bearing volume of sediment = 0.6×10^8 km^3, and contains ~10,000 Gt of methane hydrate carbon. Approximately 25% of this methane hydrate resides within continental shelf sediments at <1.2 km of ocean depth (Bratton, 1999: Fig. 1). The depth profile of these shallow methane hydrate deposits reflects the zone of greatest change in hydrate-to-gas phase boundary with increasing depth (Kvenvolden, 1988: Fig. 1), implying a reservoir most readily destabilized by the decreased depth and increased temperature associated with uplift. The sediment volume of this reservoir = 0.15×10^8 km^3, and contains ~2500 Gt of methane hydrate carbon. Given Larson’s (1991b) estimate of minimum dimension of the mid-Cretaceous superplume as 6000 by 10,000 km in size, uplift resulting from superplume mantle activity could be expected to affect at least 6×10^7 km^2 of the earth’s seafloor. The readily-destabilized reservoir of methane hydrate described above comprises 7.5% of the earth’s total seafloor, therefore a seafloor area uplifted by superplume upwelling would, on average, contain an area of readily-destabilized methane hydrate = 7.5% of the total. Using these assumptions in conjunction with estimated uplift rates for the African superplume, Fig. 3 presents the calculated amount of methane hydrate carbon liberated over 85 Myr of superplume uplift. Various geologic evidence including raised marine sediment mapping

<table>
<thead>
<tr>
<th>Magnitude of excursion (%)</th>
<th>Emission required from volcanic sources</th>
<th>Emission required from methane gas hydrate (Gt)</th>
<th>Ma of uplift (rate_l = 5 m/Ma) required for methane emission</th>
<th>Ma of uplift (rate_l = 30 m/Ma) required for methane emission</th>
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<tr>
<td><strong>Average</strong>^a^</td>
<td>24,758^d^</td>
<td>225^g^</td>
<td>60</td>
<td>10</td>
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<tr>
<td>−4.9</td>
<td></td>
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<tr>
<td><strong>Minimum</strong>^b^</td>
<td>6476^e^</td>
<td>162^h^</td>
<td>43.2</td>
<td>7.2</td>
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<tr>
<td>−3.6</td>
<td></td>
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<tr>
<td><strong>Maximum</strong>^c^</td>
<td>N.P. ^f^</td>
<td>301^i^</td>
<td>80.3</td>
<td>13.4</td>
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<tr>
<td>−6.5</td>
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^a^ Calculated atmospheric excursion is based on average δ13C for each terrestrial sample shown in Fig. 1b, including cuticle and vitrinite isolates. Values were calculated using [δ13C_{atmosphere} = (δ13C_{plant} + 18.67) / 1.10] (Arens et al., 2000).

^b^ Minimum atmospheric excursion based on variability seen in δ13C for each sample, including cuticle and vitrinite isolates.

^c^ Maximum atmospheric excursion based on variability seen in δ13C for each sample, including cuticle and vitrinite isolates.

^d^ More than a 10-fold increase in atmospheric CO2 content.

^e^ More than a 3-fold increase in atmospheric CO2 content.

^f^ Not possible, given the C isotope value of volcanic CO2 (δ13C ≈ -8; Taylor, 1986).

^g^ 2.0% Of total present-day mass of carbon stored as methane hydrate.

^h^ 1.5% Of total present-day mass of carbon stored as methane hydrate.

^i^ 2.7% Of total present-day mass of carbon stored as methane hydrate.

^j^ Based on the estimated average surface uplift rate of 5–30 m/Ma for the African superplume (Gurnis et al., 2000).
and soil erosion profiles, leads to an average surface uplift rate of 5–30 m/Ma for the Cenozoic in southern Africa due to the African superplume (Gurnis et al., 2000). If similar rates are assumed for the mid-Cretaceous superplume, a total sediment volume of 300,000–1,800,000 km³ would be uplifted in 1 Ma, which corresponds to 22,500–135,000 km³ of seafloor moved out of the stability zone of the methane hydrate sediment. Assuming all methane hydrate exiting this sediment would be converted to gaseous CH₄, this translates into a liberation of carbon from methane hydrates = 3.75–22.50 Gt for each Ma of uplift. The duration of uplift required to liberate the amount of carbon inferred from previously-discussed δ¹³C values of terrestrial sediments is listed in Table 1 and illustrated by Fig. 3. Given the range of carbon release inferred from terrestrial stable isotope data, this scenario predicts sufficient carbon release from methane hydrates for between 7.2 and 80.3 Ma of uplift. Fig. 1c illustrates the timing of key events during the early Cretaceous, including superplume origination ~9 Ma prior to the carbon isotope excursion, perhaps a sufficient period of uplift for the suggested methane hydrate carbon release during the early-Aptian.

While the discussion above demonstrates that uplift associated with superplume upwelling could have destabilized large amounts of methane hydrates during the Cretaceous, it does not, however, explain why the effect of this destabilization should be recorded as a dramatic excursion in the isotopic records. There are reasons to believe that the Cretaceous destabilization of methane hydrates occurred in a much less temporally and spatially continuous fashion than outlined presented above; for example, rates of uplift associated with extremely local upwelling have been measured to exceed 2.5 cm/year (Wicks et al., 1999), a rate three orders of magnitude larger than estimates for the Cenozoic (Gurnis et al., 2000). If such local uplift were focused upon an area particularly rich in methane hydrate, large amounts of carbon could be liberated in thousands of
years, instead of millions. Feedbacks associated with the methane hydrate release event could lead to further hydrate release as methane dissociation lowers sediment volume and results in rapid sea-level fall (Bratton, 1999), which could then trigger the dissociation of additional methane hydrates.

The most compelling possibility for a dramatic methane hydrate liberation during the Aptian involves the eruption of extensive flood basalts onto the early Cretaceous seafloor sufficiently raising sediment temperature for the destabilization of methane hydrates. The peak of magmatic activity in the Cretaceous Pacific ocean was between 120 and 80 Ma, when the Kerguelen and Ontong-Java submarine plateaus were erupted (Coffin and Eldholm, 1993) and may, therefore, have contributed to a peak methane release during the Aptian. The Ontong-Java plateau, which erupted during the Aptian-Albian, comprises a total volume of more than $1 \times 10^8$ km$^3$ of rock (Deep Sea Drilling Projects 288, 299 and Ocean Drilling Programs 803, 807 cited within Larson, 1991b), and affected at least $0.5 \times 10^8$ km$^2$ of seafloor with extremely high temperature flood basalt. If just 5% of this area contained methane hydrate at a carbon density of $1 \times 10^{19}$ g C per $0.6 \times 10^8$ km$^3$ (Fig. 2), 250 Gt of carbon from methane hydrates would be liberated from the seafloor—enough to entirely account for the isotopic excursion described above.

Fig. 3. Carbon released from methane hydrates during uplift at rates estimated for present-day southern Africa by Gurnis (2000). The gray zone represents the range of carbon from methane release inferred from $\delta^{13}C$ values in early Cretaceous terrestrial records (Fig. 1b and Jahren et al., 2001).
5. Methane in the biosphere

Although the proposed methane release to the atmosphere represents a small amount (~9%) of carbon relative to the total mass of carbon in the pre-existing Aptian atmosphere, the consequences for global biogeochemical cycling would have been extensive. Immediately after the excursion, Aptian atmospheric levels of methane would have been ~100× greater than in the present-day atmosphere (Walker, 1977). Atmospheric methane inhibits the reradiation of terrestrial infrared radiation, and so an increase in CH$_4$ would have temporarily exacerbated greenhouse conditions. Methane is removed from the atmosphere quickly through oxidation to CO$_2$ (mean tropospheric lifetime of CH$_4$ = 9.6 years). Various studies have noted that recent anthropogenic increases in methane emissions have resulted in an effective mean tropospheric lifetime of CH$_4$ that is significantly longer than the theoretical value because of non-linearities in the coupled oxidation reactions. Given these reactions, at 3× present-day methane levels “runaway growth” is predicted to occur where CH$_4$ levels will temporarily exceed the oxidizing capacity of the atmosphere, potentially triggering a warming-release feedback (Prather, 1996). The first pulses of Cretaceous “greenhouse” warming began in the late Valanginian (~14 Ma prior to the Aptian event) due to marine transgressions and generally increased thermal outputs of CO$_2$ (Lini et al., 1992). Globally warm temperatures and a low equator-to-pole thermal gradient was in place by the Albian (Spicer, 1987). The warming reached a local maximum in the early Aptian when intense warming resulted in prevalent semi-arid to arid conditions (Ruffell and Batten, 1990), I suggest that this peak in greenhouse conditions was due to methane release during what was already an established warming climate phase.

Atmospheric oxidation of methane consumes large amounts of free oxygen: at least 4 moles of O$_2$ are required to completely oxidize one mole of CH$_4$ (Cicerone and Oremland, 1988). Complete oxidation of the Aptian ~300 Gt CH$_4$ atmospheric emission would consume ~2400 Gt of O$_2$. Atmospheric O$_2$ levels during the early Cretaceous are thought to be very similar to present-day partial pressure (Berner and Canfield, 1989); the Aptian CH$_4$ emission would consume an amount of oxygen that is equal to ~0.2% of atmospheric O$_2$. It has been suggested that atmospheric O$_2$ consumption via methane oxidation has been an important process through geologic time (Watson et al., 1978), begging questions regarding the effect of atmospheric O$_2$ reduction upon particularly O$_2$-sensitive terrestrial organisms. With respect to terrestrial plants, atmospheric O$_2$ reduction would functionally increase the CO$_2$:O$_2$ mixing ratio. In the modern atmosphere, this mixing ratio ≈0.001; in the early Cretaceous, this ratio was reconstructed to be ≈0.01 (Berner, 1994; Berner and Canfield, 1989). Given the amounts of methane release and oxygen consumption presented above, methane oxidation in the early Aptian atmosphere would increase the CO$_2$:O$_2$ mixing by +0.001 as ≈825 Gt of CO$_2$ were added to the atmosphere resulting from oxidation. Models of plant community dynamics predict that at mixing ratios of ≈0.01 and above, angiosperms migrate into and become more abundant in communities previously dominated by conifers (Kienast, 1991). The earliest fossil record of flowering plants is comprised of disbursted pollen of late Valanginian age (Brenner, 1996). During the Aptian, flowering plants began the exponential phase of their taxonomic diversification and expanded from their biogeographic centers of origin (Lidgard and Crane, 1988; Penny, 1989). Angiosperms first appeared in the mid-latitude disturbed riparian communities of eastern North America during the latest Aptian (Hickey and Doyle, 1977), in the conifer-dominated forests of Victoria, Australia (Taylor
and Hickey, 1990) and southern Argentina (Romero and Archangelsky, 1986) during the middle Aptian, and in the Arctic by latest Albian (Spicer, 1990).

Brief (< 1 Ma) marine anoxic events characterize the Aptian age of the early Cretaceous (Bralower et al., 1994; Sliter, 1989; Weissert and Lini, 1991) recognized by extensive marine black shales that are anomalously rich in organic carbon. A variety of geologic processes have been explored as possible causes of deep ocean anoxia including accelerated sea-floor spreading, submarine volcanism and hydrothermal activity (Ingram et al., 1994; Larson, 1991c), sea level transgression or highstand (Bralower et al., 1994), climate fluctuation (Ruffell and Batten, 1990; Weissert and Lini, 1991), and marine oxidation of methane (Dickens et al., 1997; Hesselbo et al., 2000). Each of the above-mentioned processes represents a change in global carbon cycling that would be reflected in the atmospheric carbon pool. Methane oxidation in the water column is similar to methane combustion in that 2 moles of O$_2$ are consumed during the transformation of one mole of CH$_4$ to CO$_2$. A partitioning of methane into the ocean equal to the Aptian CH$_4$ atmospheric emission would consume an amount of oxygen that is equal to ~18% of total oceanic O$_2$, assuming O$_2$ levels in the ocean were approximately similar to present-day levels. For this reason, even a small partial amount of atmospheric methane oxidation in the oceanic water column could result in stratified oceanic anoxia. Even if atmospheric methane were not resolubilized and oxidized in the surface ocean, hydrate-released methane must traverse a long water column after escaping from sediment, prompting dissolution and oxidation of methane in the deep ocean (Kvenvolden, 1993). Highest rates of oceanic methane oxidation were measured in deep anoxic waters, even when compared to surface and near-surface waters, suggesting that methane dissolution and oxidation occur in the deep ocean up to and past the point of anoxia (Ward et al., 1987). Marine oxidation of methane has been specifically suggested as a cause of oxygen depletion in the ocean during the LPTM (Dickens, 2001; Dickens et al., 1997), and our work has suggested it as the cause of Cretaceous ocean anoxia (Jahren and Arens, 1998).

6. Conclusions

Based upon the calculations and stable isotope observations presented here, I expect that the mid-Cretaceous superplume resulted in sufficient seafloor uplift to destabilize no less than ~162 Gt of carbon from methane hydrates over ~10 Ma. In addition, eruption of the Ontong-Java flood basalts may have augmented these processes, resulting in a dramatic methane burst with magnitude approaching or exceeding that liberated by uplift. This Aptian methane hydrate dissociation first saturated the deep ocean with methane; excess methane then migrated up the water column and was released to the atmosphere, oxidized to CO$_2$ and was photosynthetically fixed by the standing terrestrial plant ecosystem. The incorporation of this isotopically light carbon from methane into marine carbonates and into the terrestrial photosynthetic biomass is evident in the marine and terrestrial isotopic excursions shown in Fig. 1a and b. Oxidation of methane within the ocean resulted in deep water anoxia, and perhaps contributed to the massive planktonic extinctions recorded during the early Cretaceous. Oxidation of methane in the atmosphere functionally changed the CO$_2$:O$_2$ mixing ratio, allowing angiosperms to displace conifers at mid- and high-latitudes, setting the stage for the angiosperm-dominated terrestrial biosphere that was to
follow. The key events are presented on a timeline against the carbon isotope record for comparison in Fig. 1. This hypothesis offers a mechanistic link between mantle processes and carbon cycling in the biosphere, and presents a congruent and unified global change scenario across earth systems within the early Cretaceous.

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