Terrestrial record of methane hydrate dissociation in the Early Cretaceous

A. Hope Jahren* Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218, USA
Nan Crystal Arens Department of Integrative Biology, University of California, Berkeley, California 94720, USA
Gustavo Sarmiento Departamento de Geociencias, Universidad Nacional, Bogotá, Colombia
Javier Guerrero Departamento de Geociencias, Universidad Nacional, Bogotá, Colombia
Ronald Amundson Division of Ecosystem Science, University of California, Berkeley, California 94720, USA

*E-mail: jahren@jhu.edu.

INTRODUCTION
The total present-day mass of carbon stored as methane hydrate is thought to be large (11 000 Gt of C) (1 Gt C = 10¹⁵ g C) and very ¹³C depleted (δ¹³C ≈ −60‰) (Kvenvolden, 1993). Processes as diverse as gradual pressure increase due to sedimentary burial, submarine slope failure, sea-level regression, or increase in bottom water temperatures could induce rapid liberation of CH₄ (Kvenvolden, 1993). The carbon isotope signature of methane dissociation into local seawater and ultimately to the atmosphere would be reflected in the δ¹³C of the actively cycling carbon pools.

A methane release from ocean hydrates at the late Paleocene thermal maximum (55.6 Ma) has been inferred from a negative excursion (Δ = −2.5‰) in the marine carbonate record (Dickens et al., 1995, 1997). This anomaly was correlated to a negative excursion of similar magnitude in the terrestrial record; i.e., soil carbonate δ¹³C (Koch et al., 1995) and terrestrial organic matter δ¹³C (Stott et al., 1996). Recent work has confirmed that the global biogeochemical response to such an event is extremely rapid (Norris and Rohl, 1999), and changes in the δ¹³C of atmospheric CO₂ have been shown to reflect source-specific changes in global carbon cycling (Peng et al., 1983). Plant compression fossils are useful isotopic substrates because land plants sample the atmosphere directly and in a predictable way during photosynthetic carbon fixation. Our work applies a recently developed relationship between the δ¹³C of C₃ vascular land plant tissue and the δ¹³C of atmospheric CO₂ (Arens et al., 2000) to estimate changes in the δ¹³C of atmospheric CO₂ through the Early Cretaceous and discusses implications for biogeochemical cycling in the early Aptian (ca. 117 Ma).

SAMPLES AND METHODS
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, was isolated and analyzed for C isotope ratios. The three localities are within 100 km of one another and constitute ∼2250 m of section within the same biostratigraphic province. Units sampled include the Une, Fômeque, and Las Juntas Formations, which encompass an 18 m.y. interval during the Early Cretaceous with no evidence of depositional disconformity. Age dates were based on biostratigraphic correlation with well-established dinoflagellate and ammonite zones (Guerrero and Sarmiento, 1996). All samples were analyzed for δ¹³C of bulk organic material, and only strata bearing abundant land-plant macrofossils were analyzed. For bulk organic material determinations, a 1–5 g sample of the rock was subsampled and immersed in 1 M HCl overnight to remove carbonate. The remaining bulk organic residue was analyzed for δ¹³C in triplicate. To address the possible incorporation of any carbon derived from other than terrestrial productivity, we isolated two components specific to vascular land plants: vitrinite and cuticle. Vitrinite is the coalified remains of highly lignified plant tissues, primarily xylem; cuticle is a waxy compound that coats plant epidermal surfaces. Both materials are restricted to vascular land plants and represent uniquely terrestrial carbon compounds that can be recognized at low magnification. Vitrinite and cuticle isolates were collected and prepared directly from abundant fern and cycad fossils when possible; when no suitable fossils were available, rock was acid macerated (HF and HCl), rinsed, and handpicked. In this case, isolated tracheids and cuticle could not be identified to taxon. Vitrinite was isolated and manually separated via its color, texture, and fracture in rock hand specimens; it was then soaked in 60% HF overnight to remove any inorganic components. In some cases, clumps of tracheids were isolated from rock macerate after HF treatment. Cuticle was isolated after exposure to 60% HF via manual separation at 5× magnification; cuticle morphology was verified under 40× magnification. Vitrinite and cuticle C isotope determinations were made in duplicate and triplicate when sufficient material could be isolated.

All organic carbon samples were prepared for stable isotope analysis via combustion in sealed tubes containing Cu, CuO, and Ag. Released CO₂ was purified and collected for ¹³C/¹²C measurement on the mass spectrometer. All isotope values are reported in delta notation relative to the Vienna Pee Dee belemnite standard (VPDB).

RESULTS
The C isotope data from the sections are presented in Figure 1A. Bulk δ¹³C values range from −22‰ to −24‰ during the late Valanginian, through the Hauterivian and early Barremian. Values increase in the late Barremian (δ¹³C ≈ −21‰), followed by a dramatic decrease to −28‰ in the early Aptian, which is followed by a sharp increase to −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 compose ∼100 m of sediment (application of average sedimentation rates for the Fômeque Formation suggest that this event was <1 m.y. in duration). Multiple studies have shown that decomposition does not usually alter the δ¹³C of plant tissues by more than 2‰; accordingly,
ly, the maximum difference seen between bulk organic matter $\delta^{13}$C and lignin and cuticle isotope $\delta^{13}$C approaches 2‰. The congruence of bulk organic, cuticle, and vitrinite $\delta^{13}$C affirms the bulk organic carbon signal is primarily derived from land-plant organic input. Alteration of organic constituents was evaluated using the thermal alteration scale (Batten, 1996); all constituents were within low-maturation categories 4 and 5, suggesting maximum burial of 3 km and maximum temperatures of 70 °C. Regression analysis of $\delta^{13}$C against the maturation estimates showed no significant relationship, suggesting that patterns observed in $\delta^{13}$C through time are not perturbed by differing thermal histories of the rocks. In addition, the similarity in degree of thermal maturity throughout the section supports the conclusion that patterns observed in $\delta^{13}$C through time reflect genetic, rather than diagenetic, phenomena.

We reconstruct the $\delta^{13}$C record of the atmosphere (Fig. 2) using the average $\delta^{13}$C of strata within these terrestrial sediments, including isolated cuticle and vitrinite, components unique to land plants. Cretaceous ecosystems were dominated by C3 plants (Bocherens et al., 1993); isotopic fractionation during C3 photosynthesis is influenced by differential diffusion of $^{12}$CO$_2$ versus $^{13}$CO$_2$ in air; discrimination imparted by the primary carbon fixation enzyme, and ecophysiological factors that balance leaf carbon gain with water loss (Farquhar et al., 1989, reviewed in Arens et al., 2000). With notable exceptions (Gröcke et al., 1999), land plants have been overlooked as a source of information about the isotopic composition of atmospheric CO$_2$ because these ecophysiological vital effects were believed to swamp the atmospheric signal (reviewed in Farquhar et al., 1989). However, in an analysis of a large data set (519 published $\delta^{13}$C$_{plant}$ measurements on 176 C3 species) Arens et al. (2000) showed that the relationship between the $\delta^{13}$C of plant tissue and atmospheric CO$_2$ is linear and significant ($r^2 = 0.91$ for the full data set). Using a subset of these data, Arens et al. (2000) proposed an empirically derived relationship ($\delta^{13}$C$_{atmosphere} = [\delta^{13}$C$_{plant} + 18.67]/1.10$) that could be used to estimate the $\delta^{13}$C of atmospheric CO$_2$ from preserved terrestrial plant material. Arens et al. (2000) quantified the error due to vital effects for the large set of species and ecological conditions studied (calculated here as a 99% confidence interval). In a realistic test to verify the predictive ability of this method, Arens et al. (2000) showed that for most mesic environments, the relationship predicted both ancient and modern atmospheric $\delta^{13}$C within the defined confidence interval.

Our analyses of bulk organic carbon reflect an ecosystem average signal of rapidly buried land-plant organic material; palynology of these sediments indicates moderate palyno-species richness and does not show major changes in the taxonomic composition or relative abundance of plant groups during the interval studied (Arens, 1996). Therefore, the significant $\delta^{13}$C excursions observed in this sequence cannot be explained by changing floristics that might add new physiologies or climate-selected ecologies into the material preserved.

**DISCUSSION**

The striking negative excursion ($\Delta = -5$‰) inferred in atmospheric CO$_2$ $\delta^{13}$C in the early Aptian, followed by a rapid positive compensation ($\Delta = +5$‰) during the mid-Aptian (Fig. 2), suggests substantial disruption in global carbon cycling. Several sources of isotopically light carbon must be considered to identify the process underlying this atmospheric excursion: magmatically derived CO$_2$, volatilized organic carbon from standing or buried biomass, and methane. Cretaceous $p$CO$_2$ was modeled to be about four times present-day partial pressure ($p$) (Bernier, 1990), suggesting an atmosphere containing $\sim$2400 Gt of carbon. Using this assumption, the following source-mixing analysis was used to estimate the amount of carbon ($n$) required from each of the potential sources to drive the negative atmospheric excursion: $2400 + n$ Gt C $\cdot$ ($\delta^{13}$C$_{atmosphere}$ early Aptian = $2400$ Gt C $\cdot$ ($\delta^{13}$C$_{plant}$) + $n$ Gt C $\cdot$ ($\delta^{13}$C$_{emission}$). These calculations (Table 1) indicate that the Aptian atmospheric excursion described here would require more than a 10-fold increase in atmospheric CO$_2$ with magmatically derived CO$_2$ ($\delta^{13}$C $\sim -8$; Taylor, 1986), making volcanic CO$_2$ an untenable carbon source, despite abundant evidence for enhanced volcanism during the Aptian. If volatilized organic carbon were the source of $^{13}$C-depleted CO$_2$ ($\delta^{13}$C $\sim -25$; Peng et al.,

Figure 1. $\delta^{13}$C data from Cretaceous: terrestrial and marine organic carbon (1A) and marine carbonate (1B) analyses. Overall time scale presented here is based on Harland et al. (1989); marine and terrestrial records cross-correlate to $\pm$1 m.y.
### 1.5% of total present-day mass of carbon stored as methane hydrate.

$^2$ More than the total amount of carbon stored in living terrestrial plants.

### 77% of the total amount of carbon stored in living terrestrial plants.

### 2.0% of total present-day mass of carbon stored as methane hydrate.

** More than the total amount of carbon stored in living terrestrial plants.

§§§ More than the total amount of carbon stored in living terrestrial plants.

# More than a 10-fold increase in atmospheric CO$_2$ content.

- Calculated excursion is based on average $^{13}$C for each sample, including cuticle and vitrinite isolates.
- Minimum excursion based on variability seen in $^{13}$C for each sample, including cuticle and vitrinite isolates.
- Maximum excursion based on variability seen in $^{13}$C for each sample, including cuticle and vitrinite isolates.
- More than a 10-fold increase in atmospheric CO$_2$ content.
- More than the total amount of carbon stored in living terrestrial plants.
- 2.0% of total present-day mass of carbon stored as methane hydrate.
- More than a 3-fold increase in atmospheric CO$_2$ content.
- 77% of the total amount of carbon stored in living terrestrial plants.
- 15% of total present-day mass of carbon stored as methane hydrate.
- Not possible, given the assumed $^{13}$C of volcanic CO$_2$.
- More than the total amount of carbon stored in living terrestrial plants.
- 1.5% of total present-day mass of carbon stored as methane hydrate.

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1983), $-677$ Gt of carbon would be required to produce the observed excursion, more than all the carbon stored in today’s terrestrial vegetation (Sundquist, 1993). A rapid ($<1$ m.y.) volatilization of a significant portion of Aptian terrestrial biomass would result in major floristic and terrestrial facies changes. Early Cretaceous flora was changing in response to the biogeographic expansion of angiosperms (discussed in the following) and the onset of the Cretaceous greenhouse (Crane and Lidgard, 1989), but there is no evidence of rapid or catastrophic tempo to these transitions, nor does the Aptian sedimentary record contain unusual amounts of charcoal (Chaloner and McElwain, 1997).

In contrast, a relatively small contribution of methane from methane hydrates could have produced the Aptian atmospheric excursion. A contribution to the atmosphere of only $\sim225$ Gt of carbon from methane hydrate, equal to 2% of the present-day oceanic reservoir, could account for the excursion. Methane hydrate stability in sediment pore spaces partially depends on temperature, and warming could induce catastrophic liberation (Dickens et al., 1995). The first pulses of Cretaceous greenhouse warming began in the late Valanginian $(\sim13$ m.y. prior to the negative excursion shown in Fig. 2) (Lini et al., 1992), and may have contributed to the destabilization and subsequent liberation of accumulated methane hydrate.

Although the amount of carbon released from methane hydrates need only have been small $(\sim9\%)$ relative to the total mass of carbon in the preexisting Aptian atmosphere, the consequences for global biogeochemical cycling would have been extensive. To account for the negative isotopic excursion, $\sim300$ Gt of CH$_4$ would have to be liberated to the Aptian atmosphere. Atmospheric methane inhibits the reradiation of terrestrial infrared radiation, and so an increase in CH$_4$ would have temporarily exacerbated greenhouse conditions. Intense continental-scale warming in the early Aptian has been inferred from terrestrial secondary minerals (Ruffel and Batten, 1990). Hydrate-released methane must traverse a long water column after escaping from sediment, prompting dissolution and oxidation of methane in the ocean (Kvenvolden, 1993). Widespread deposition of black shales has been observed in the Early Cretaceous marine record (e.g., Bralower et al., 1994; Menegatti et al., 1998); these shales are sometimes interpreted as the result of marine anoxic events (Sliter, 1989). We expect that methane hydrate dissociation during the Early Cretaceous first saturated the deep ocean with methane, perhaps resulting in anoxia; excess methane then migrated up the water column and was released to the atmosphere, oxidized to CO$_2$, and photosynthetically fixed by the standing terrestrial plant ecosystem. Figure 1B presents $^{13}$C$_{\text{carbonate}}$ from Deep Sea Drilling Project Hole 534 (Robertson and Bliefeick, 1983) and from outcrop data that have been correlated to standard microfossil zones (Weissert, 1989); in addition, three high-resolution records of marine $^{13}$C$_{\text{carbonate}}$ are presented for the Aptian (Jenkyns, 1995; Menegatti et al., 1998; Scholle and Arthur, 1980). Comparison of the terrestrial versus marine records has been established as a means to examine carbon reservoir shifts (Koch et al., 1992); inspection of these curves in the Early Cretaceous (Fig. 1) reveals similar trends in both records, but lower response magnitude in the marine record. Most notable is the apparent 3.0% decrease (Bralower et al., 1999) indicated in the marine organic carbon record during the Aptian (Fig. 1A).

Methane oxidation in the atmosphere results in a net consumption of 4 moles of O$_2$ for every mole of CH$_4$ oxidized: complete oxidation of the Aptian $\sim300$ Gt CH$_4$ atmospheric emission would consume $\sim2400$ Gt of O$_2$. Atmospheric O$_2$ levels during the Early Cretaceous are thought to be very similar (i.e., 28% $\pm$ 4% of the atmosphere) to present-day
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