

# Compound-specific carbon isotopes from Earth's largest flood basalt eruptions directly linked to the end-Triassic mass extinction

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A leading hypothesis explaining Phanerozoic mass extinctions and associated carbon isotopic anomalies is the emission of greenhouse, other gases, and aerosols caused by eruptions of continental flood basalt provinces. However, the necessary serial relationship between these eruptions, isotopic excursions, and extinctions has never been tested in geological sections preserving all three records. The end-Triassic extinction (ETE) at 201.4 Ma is among the largest of these extinctions and is tied to a large negative carbon isotope excursion, reflecting perturbations of the carbon cycle including a transient increase in CO<sub>2</sub>. The cause of the ETE has been inferred to be the eruption of the giant Central Atlantic magmatic province (CAMP). Here, we show that carbon isotopes of leaf wax derived lipids (*n*-alkanes), wood, and total organic carbon from two orbitally paced lacustrine sections interbedded with the CAMP in eastern North America show similar excursions to those seen in the mostly marine St. Audrie's Bay section in England. Based on these results, the ETE began synchronously in marine and terrestrial environments slightly before the oldest basalts in eastern North America but simultaneous with the eruption of the oldest flows in Morocco, a CO<sub>2</sub> super greenhouse, and marine biocalcification crisis. Because the temporal relationship between CAMP eruptions, mass extinction, and the carbon isotopic excursions are shown in the same place, this is the strongest case for a volcanic cause of a mass extinction to date.

astrochronology | CO<sub>2</sub> | Jurassic | large igneous provinces | *n*-alkane

Plants record through photosynthetic pathways the atmospheric values of  $\delta^{13}\text{C}$  that in turn reflect the exchangeable surface oceanic carbon reservoir (1). One of the most direct known plant proxies is the  $\delta^{13}\text{C}_{\text{alk}}$  measurements of *n*-C<sub>25</sub>–*n*-C<sub>31</sub> *n*-alkanes derived from leaf wax lipids of plant cuticles (2). We analyzed  $\delta^{13}\text{C}_{\text{alk}}$ , the carbon isotopic composition of wood ( $\delta^{13}\text{C}_{\text{wood}}$ ), and total organic carbon ( $\delta^{13}\text{C}_{\text{toc}}$ ) from sediments from two overlapping lacustrine sections interbedded with the lavas of the Central Atlantic magmatic province (CAMP) (3) in eastern North America to obtain a carbon isotope record unambiguously tied to the eruptions and climate proxies to compare with and calibrate organic carbon and carbonate  $\delta^{13}\text{C}$  records from elsewhere (3–7). This allows direct determination of the relationship between one of the largest Phanerozoic mass extinctions, the end-Triassic extinction (ETE) (8), carbon isotopic and CO<sub>2</sub> (9) excursions, the biocalcification crisis (10), and their proposed cause, the CAMP (3, 11–13). Core and outcrop samples were obtained from the Newark (New York, New Jersey, and Pennsylvania) and Hartford (Connecticut and Massachusetts) rift basins at 19–20° N paleolatitude (14) in the tropical humid to arid transition of central Pangea (Fig. 1). A hierarchy of Milankovitch-forced lake level cycles permeate the sampled strata in these basins, and in conjunction with a high sediment accumulation rate and magnetostratigraphic and radioisotopic calibration (*SI Text* and *Datasets S1–S3*), a 2.4 m.y. unbroken record of events

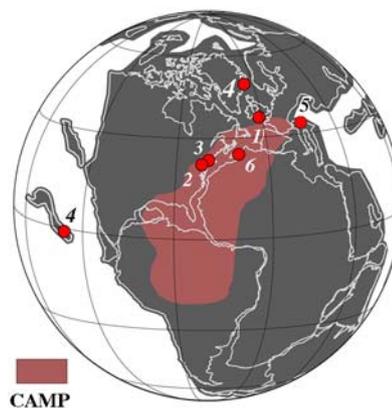


Fig. 1. Map of Pangea at 201 Ma showing the distribution of the CAMP and the localities discussed in the text: 1, St. Audrie's Bay; 2, Newark basin; 3, Hartford basin; 4, Kennecott Point; 5, Val Adrara; 6, Moroccan CAMP sections. Base map (orthographic projection) courtesy of C. Scotese based on the latitudinal positions of ref. 14.

surrounding the ETE can be placed into the high-precision (<20 ky) Newark/Hartford basin astronomically calibrated geomagnetic polarity time scale (NBAGPTS) (15–17) (Fig. 2). The combined section is registered to the marine record by high-resolution magnetostratigraphy (17, 18), high-precision U–Pb ages, and cyclostratigraphy (7, 19), and spans the late Rhaetian of the Late Triassic to the early Sinemurian of the Early Jurassic (Fig. 2). Our data indicate the *n*-alkanes from these strata preserve an original leaf wax signal (*SI Text*).

## Carbon Isotope Results

All three sets of carbon isotopic data from the Newark and Hartford basin sections show considerable variability seemingly tied in part to the lacustrine cyclicity (spanning approximately 9‰ in  $\delta^{13}\text{C}_{\text{alk}}$ , approximately 7‰ in  $\delta^{13}\text{C}_{\text{wood}}$ , and approximately 15‰ in  $\delta^{13}\text{C}_{\text{toc}}$ ) through the section, but show largely parallel trends around the ETE (Fig. 2). Specifically, there is an approximately 2–4‰ shift to <sup>13</sup>C-depleted values exactly at the ETE and associated fern spike (16) as reflected in the Newark and Hartford basins. The duration of this distinct excursion in the Newark and Hartford basins is only about 20–40 ky. This is succeeded by a distinct <sup>13</sup>C-enriched interval (by approximately

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a change in contribution of different organisms, a possibility suggested for the origin of the initial excursion at other localities (6). Thus, a change in community structure is likely responsible for at least part of the initial excursion as seen at the St. Audrie's Bay section. This interval shows an unusual abundance of fern spores but no exceptional concentration of organic-walled aquatic organisms at St. Audrie's Bay (20), suggesting a terrestrial ecosystem change. The duration of the initial excursion at St. Audrie's Bay has been independently estimated at 20–40 ky (7) in agreement with our estimates based on the Newark–Hartford data.

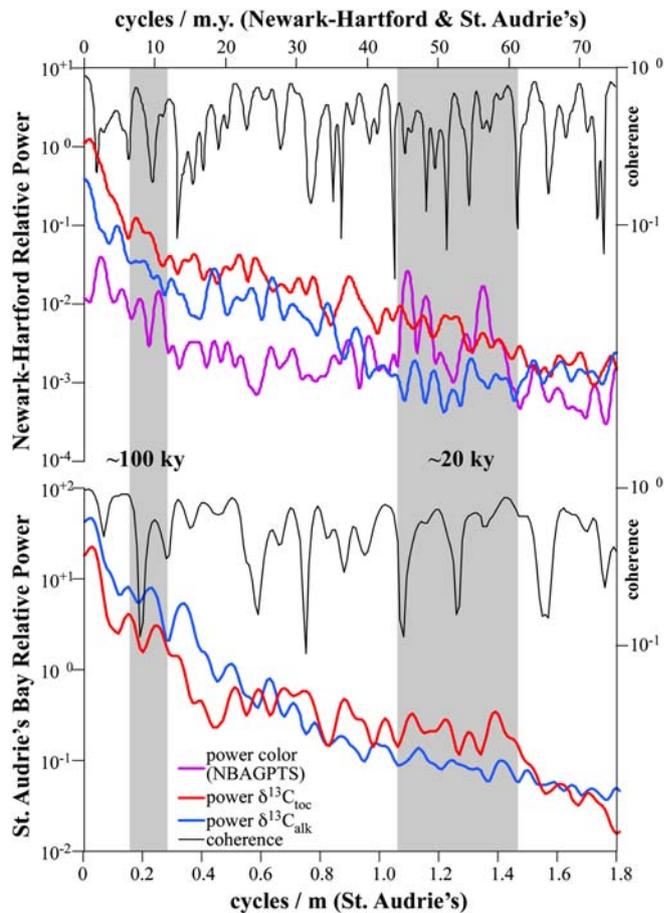
The initial excursion thus can be identified as beginning at the extinction level in the Newark basin possibly extending through the time of the deposition of the oldest CAMP lava flows. Critically, extinctions persist into strata postdating the initial excursion (e.g., conodonts) at St. Audrie's Bay (20) and elsewhere, demonstrating that extinctions persisted a short time after the initial CAMP pulse.

## Discussion

Both the combined Newark and Hartford  $\delta^{13}\text{C}_{\text{alk}}$  and the St. Audrie's Bay  $\delta^{13}\text{C}_{\text{alk}}$  data exhibit oscillations in values younger and older than the initial excursion that are not directly connected with extinctions, but rather track the lacustrine cyclicity and exhibit coherent power around an approximately 100 ky periodicity (Fig. 3) (SI Text).  $\delta^{13}\text{C}_{\text{alk}}$  and  $\delta^{13}\text{C}_{\text{toc}}$  are also coherent around approximately 100 ky. The magnitude of these oscillations decreases after the positive excursion following the initial excursion, and we suggest they reflect climate-related ecological changes altering both the taxonomic composition of the plant communities supplying the waxes and the isotopic discrimination of the members of the community under highly stressed conditions. With only the two available fiducials (the ETE and the Sinemurian–Hettangian boundary), the St. Audrie's  $\delta^{13}\text{C}_{\text{alk}}$  and  $\delta^{13}\text{C}_{\text{toc}}$  data also exhibit coherent approximately 100 ky periodicity using the NBAGPTS for temporal constraints. The thickness periodicities are also fully consistent with those seen in  $\delta^{13}\text{C}_{\text{toc}}$ , percent total organic carbon, and percent carbonate described in ref. 7 (Fig. 3), again very strongly suggesting that both the time scale and the correlation between the two sections are correct.

Although the isotopic excursion and ETE predate the onset of CAMP in the Newark and Hartford basins, the lava flows in these basins do not reflect the full temporal extent of the eruptions. The Culpeper basin of Virginia and Argana and Central High Atlas basins of Morocco demonstrate that the CAMP eruptions were more extensive than the three flow sequences preserved in the Newark and Hartford basins (23) (Fig. 4). In addition, some CAMP flows in Morocco are most likely slightly older than those recognized in eastern North America (24, 25) (SI Text). These older flows may be synchronous with the initiation of the ETE.

It is unlikely that the initial excursion seen at St. Audrie's Bay and in eastern North America was generated by mantle  $\text{CO}_2$  alone, because of the similarity in atmospheric and mantle  $\delta^{13}\text{C}$  values (26). Hence, an injection of  $^{12}\text{C}$  carbon from CAMP-triggered methane clathrates (4, 9) dissociation or thermogenic methane (27) release from intrusive metamorphism (13) has been hypothesized. One alternative is that an intensification of the hydrological cycle, as a result of greater  $\text{CO}_2$ -forced warming causing an increase in available moisture driving greater isotopic discrimination (28) caused a shift toward more  $^{13}\text{C}$ -depleted values in the plant wax *n*-alkanes. This is entirely consistent with the enhanced lacustrine cyclicity and *n*-alkane cyclicity in the Newark and Hartford data after the ETE. A concurrent shutoff of the biological pump would result in a homogenization of the water column caused by the extinction of zooplankton grazers (cf. K-T boundary in ref. 29) with surface waters becoming enriched in  $^{12}\text{C}$ . The short duration of the initial excursion is also incompatible with the modeled estimates of the



**Fig. 3.** Comparison between power spectra of carbon isotopic data from the Newark and Hartford basins and the St. Audrie's Bay section using the same time scale (NBAGPTS) based on the correlation to the base of the ETE and the Hettangian–Sinemurian boundary. Note the correspondence between the approximately 100 ky periods in  $\delta^{13}\text{C}_{\text{alk}}$  and  $\delta^{13}\text{C}_{\text{toc}}$  in both the Newark–Hartford and St. Audrie's data and the presence of the approximately 20 ky cycle in the St. Audrie's  $\delta^{13}\text{C}_{\text{toc}}$  data. Coherence in the Newark–Hartford data and in the St. Audrie's data is shown between the  $\delta^{13}\text{C}_{\text{alk}}$  and  $\delta^{13}\text{C}_{\text{toc}}$  with the spectrum for color shown for reference as it is tuned to the NBAGPTS. Nonzero coherence is greater than 0.6.

recovery time from a methane clathrates dissociation event by over an order of magnitude (20–40 ky compared to 700–1000 ky from ref. 26). Other proposed killing mechanisms include CAMP-outgassed or metamorphism-related volatiles such as sulfuric acid (27) or halogens (13, 30); however, none of these models have yielded unique predictions testable in the sedimentary record. We also cannot exclude a role for a bolide impact as a killing mechanism, although evidence consisting mostly of modest Ir anomalies (16) is also compatible with a volcanic origin.

Carbonate  $\delta^{13}\text{C}$  records from St. Audrie's Bay (31) track the  $\delta^{13}\text{C}_{\text{toc}}$  and  $\delta^{13}\text{C}_{\text{alk}}$  data, which in turn match the variations in the Newark and Hartford  $\delta^{13}\text{C}_{\text{alk}}$  data that are orbitally paced. Because the St. Audrie's Bay carbonate data are unlikely to have been affected by local community change without some process linking them via the exchangeable carbon reservoirs, there seems to have been a significant role for orbital cycles pacing the Earth's exchangeable reservoirs as has been suggested for a number of other isotopic excursions (32). However, the behavior of *n*-alkanes in the initial excursion is qualitatively different from the other fluctuations, suggesting a different origin such as the effects of the initial influx of greenhouse gases and the extinctions themselves, the exact expression of which would be influenced by synergetic changes in the local conditions and local communities



The negative  $\delta^{13}\text{C}$  excursions in the Newark, Hartford, and St. Audrie's Bay documented by the *n*-alkane, wood, total organic carbon data, and the correlations to Jamesonland strongly suggest a massive input of  $^{13}\text{C}$ -depleted  $\text{CO}_2$  and/or other greenhouse gases coincident with the onset of CAMP. The very tight association between the onset of the CAMP and the abrupt extinctions in the tropics and subtropics, the more protracted extinctions well into the CAMP episode in the higher latitudes during the time of maximum eruptive rate, and the association of the elevated  $\text{CO}_2$  levels tied to the entire known CAMP episode strongly argues for a major causative role for CAMP-generated  $\text{CO}_2$  in the extinctions themselves. Our interpretation of the carbon isotopic data from these continental and marine sections provides strong direct evidence by direct superposition that the eruption of a giant flood basalt province could cause a climatic catastrophe resulting in a major mass extinction.

## Methods

For *n*-alkane extraction, approximately 4–12 g of powdered sedimentary rock samples were extracted on a Dionex Accelerated Solvent Extraction system using three washes of dichloromethane (DCM) or 9:1 DCM/methanol to produce a total lipid extract (TLE). The TLE was saponified with 0.5N KOH/methanol, and then extracted with hexane. This neutral extract was dried with anhydrous  $\text{Na}_2\text{SO}_4$  to remove traces of water, then eluted from a silica gel column (1 mL bed volume, silica gel 2% deactivated) into two fractions, first a hexane elutable and second a combined DCM and methanol elutable fraction. If required, the hexane elutable fraction was further fractionated into adduct [straight chain ( $\text{C} \geq 14$ ) *n*-alkanes] and nonadduct fractions by urea adduction, or by sequestering the straight chain alkanes in zeolites, rinsing with hexane, and alkane recovery by dissolution of the zeolite with aqueous HF.

Compound-specific carbon isotopic measurements were determined by isotope ratio monitoring–gas chromatography/mass spectrometry using a Thermo DeltaVPlus MS coupled to an Agilent 6890 GC via a GCC-III combustion interface at Brown University. The  $\delta^{13}\text{C}$  values for individual compounds were determined based on introduction of reference  $\text{CO}_2$  gas pulses (previously and subsequently calibrated with a series of well-characterized standard materials), reported as means of duplicate runs ( $\sigma = \pm 0.3$  to 0.6), and expressed in ‰ relative to the Pee Dee belemnite (PDB). The bulk organic matter of sediment wood was analyzed to determine the ratio of  $^{13}\text{C}/^{12}\text{C}$  by mass spectrometry. The samples were cleaned with deionized water, air-dried, ground into a fine powder with a ceramic mortar and pestle, fumed with 37% HCl in a bell jar at 60 °C for 50 h (to remove recalcitrant carbonate), and dried above a plate of silica gel desiccant at 60 °C for at least 24 h. All samples were weighed into silver capsules, with mass determined by total organic-carbon (TOC) content, grouped according to TOC, and processed with an automated micro-Dumas combustion technique using a Europa ANCA system plumbed into a 20-20-NT continuous flow mass spectrometer system at Lamont-Doherty Earth Observatory. C isotope ratios were measured against National Institute of Standards and Technology and International Atomic Energy Agency standard reference materials and combusted in the same manner as the samples (glucosamine,  $\delta^{13}\text{C} = -20.80$ , C = 20.50%; methionine,  $\delta^{13}\text{C} = 25.10$ , C = 40.25% (Cornell only), all versus the PDB ( $^{13}\text{C}/^{12}\text{C} = 11237.2 \pm 60 \times 10^{-6}$ ). Precision of the analytical system is 0.12‰ for C at the typical sample sizes (4  $\mu\text{m}$  C) used here.

Time series analysis was performed using Analyseries 2.037 (37).

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