Evidence of Volcanic Sulfate Aerosols from Two Early Jurassic Eruptions of the Central Atlantic Magmatic Province (CAMP, Eastern North America)

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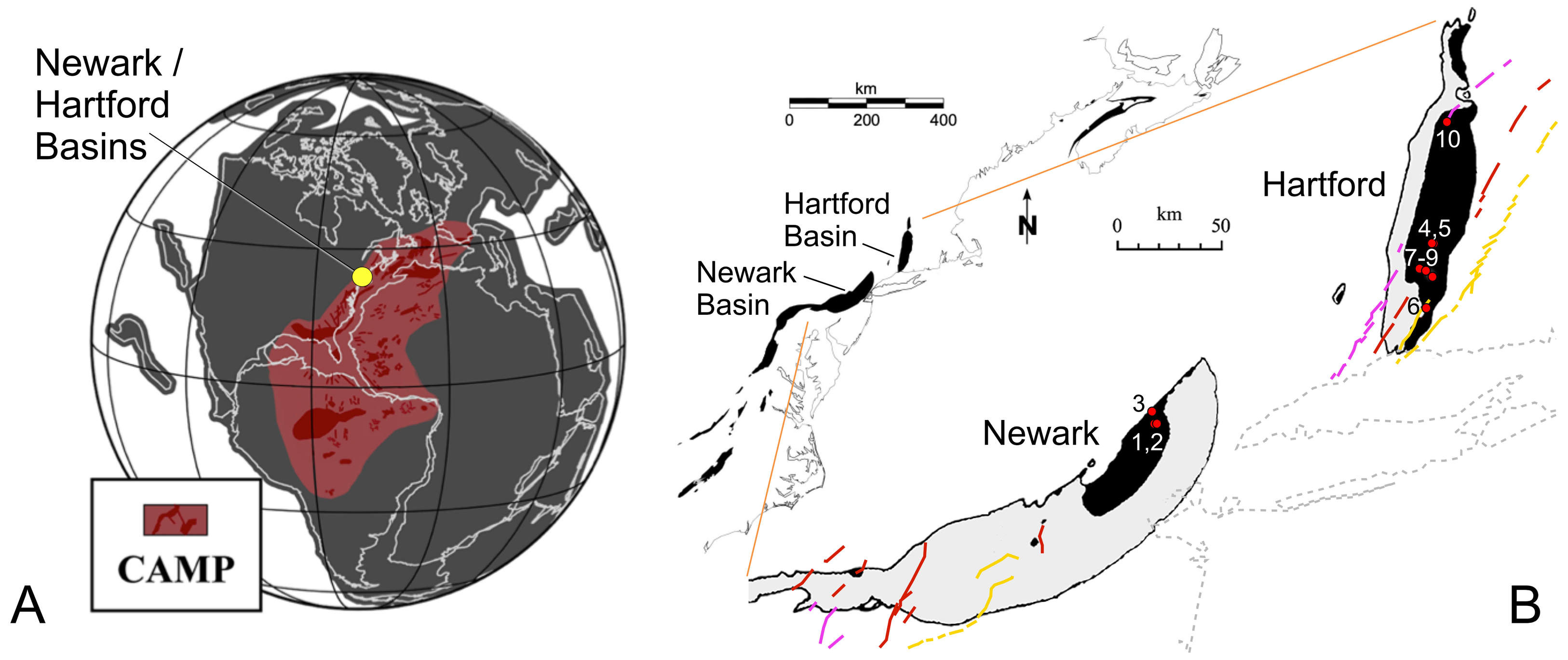
Abstract

Two small airfalls (Pompton ashes) occur in a deep-water phase of a single climatic precession-paced lacustrine cycle at ten localities in the Hartford and Newark rifts in eastern North America (1). Strata adjacent to these ashes have sulfur isotopic ratios consistent with an input of volcanic aerosol sulfate. Two cores of this cycle in the Towaco Fm of the Newark Basin (2), show an average background $\delta^{34}S_{pyrite}$ of ~0‰ in gray, shallow-lake strata that bracket a black, highstand bed. Most of the latter is characterized by a dramatic excursion in $\delta^{34}S_{pyrite}$ to between +40‰ to +60‰ interpreted as due to closed-system microbial sulfate reduction in a progressively ^{34}S-enriched reservoir. As this lake filled and reached its outlet during its early hydrologically open phase, the basal microlaminated, fish-bearing basal layers of the highstand bed would be expected to remain ~0‰ $\delta^{34}S_{pyrite}$. Instead, $\delta^{34}S_{pyrite}$ became more depleted than anywhere else in the cycle (-20‰) suggesting an input of sulfate into the lake. This same negative excursion is also seen at two outcrops of the East Berlin Fm of the Hartford Basin. As this is the exact interval hosting the Pompton ashes at all sites, we hypothesize that this negative excursion was a consequence of direct inputs of volcanic aerosols from eruptions and subsequent drainage of airfall sulfate from the surrounding watershed that diffused into porewaters. Presumably, the airfalls immediately preceded volcanic winters.

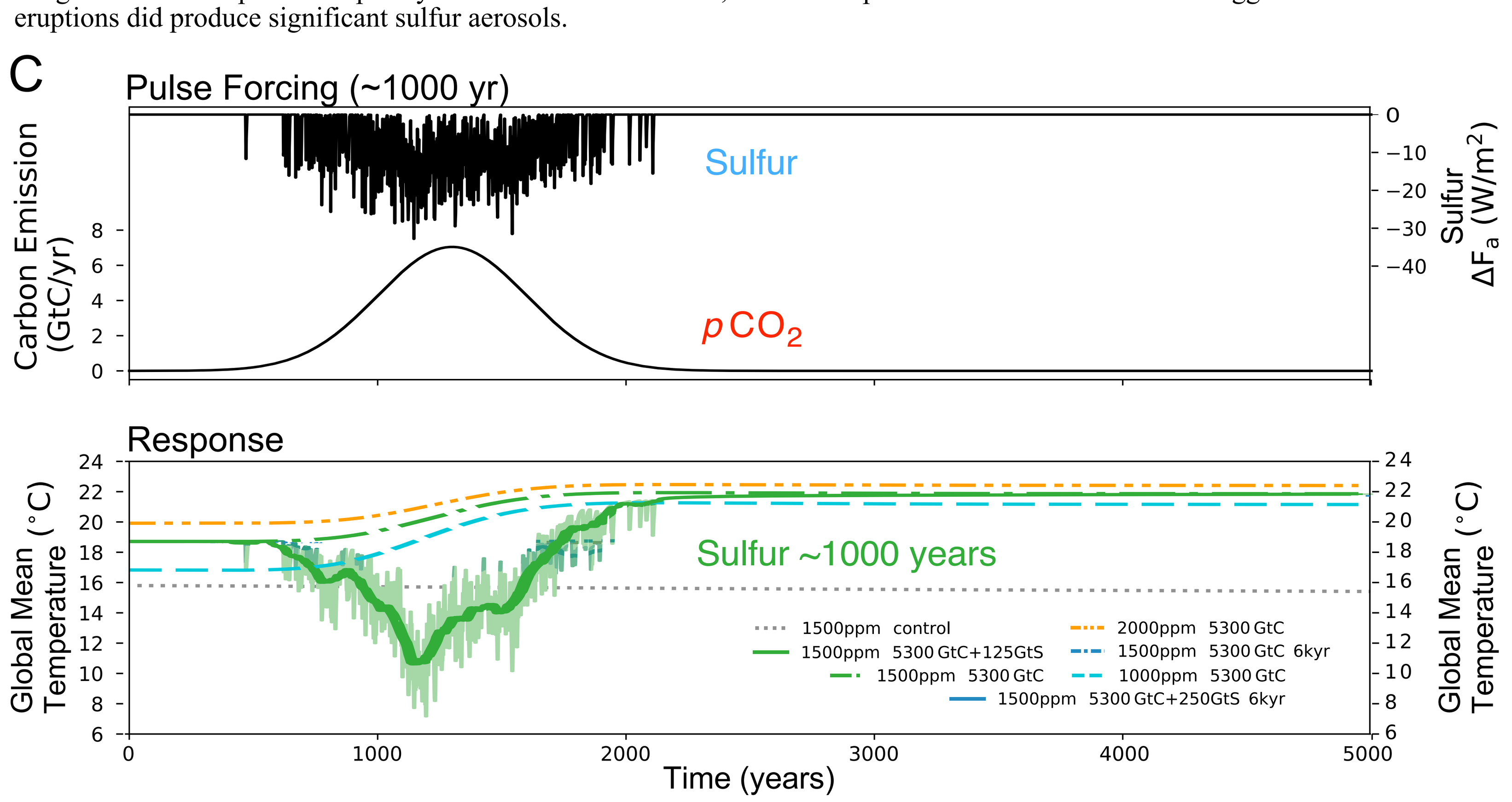
There are 8 other similar lacustrine cycles in the Towaco and East Berlin Fms (3) that can provide independent tests of this hypothesis. We predict that most will lack a negative excursion in the deepening phases of the lakes, but will show strong positive excursions as the lakes became hydrologically closed and $\delta^{34}S_{pyrite}$ was dominated by reservoir effects. Conversely, large negative $\delta^{34}S_{pyrite}$ excursions should characterize the basal East Berlin Fm deposited during CAMP lava eruptions that have been hypothesized to produce the kind of intense volcanic winters that drove the continental expression of the end Triassic extinction (4).

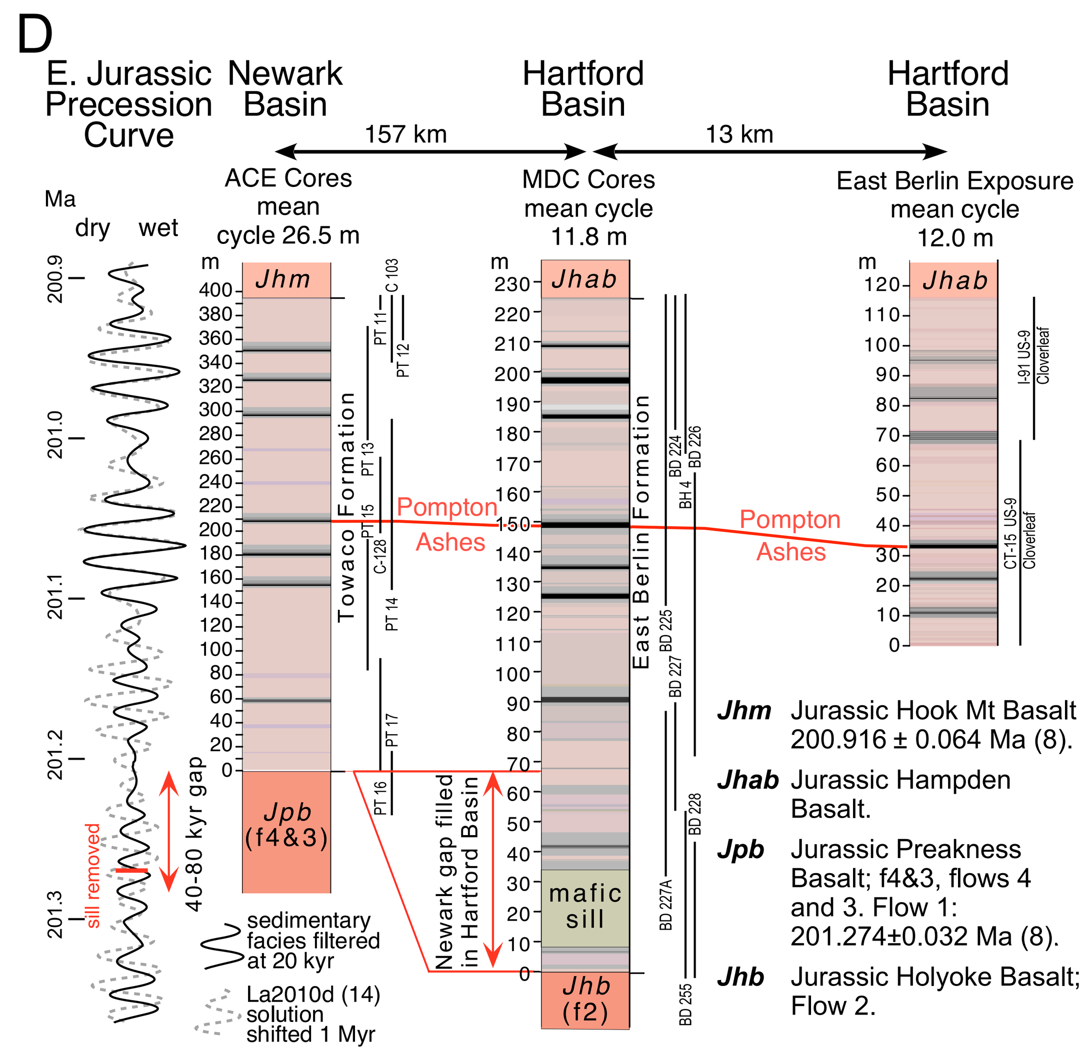
Summary: Sulfur isotopes from an Early Jurassic lake sediment interval suggest sulfate aerosol input from two eruptions of the giant Central Atlantic Magmatic Province, plausibly associated with volcanic winters of the kind that caused end Triassic mass extinction. The eruptions produced two thin airfall ashes found at 10 localities in two rift basins in eastern North America spanning over 200 km, dating from 201 million years ago.



The Central Atlantic Magmatic Province (CAMP) (5) (**Fig. A**) is the areally largest continental flood basalt complex on Earth. Like several other continental large igneous provinces (6), the CAMP is strongly implicated in a mass extinction, in this case, the End-Triassic mass extinction (ETE) at 201.6 Ma (7, 8). Although global warming and ocean acidification from CAMP-related pCO_2 inreases are plausible mechanisms for the biotic crisis in the oceans (9, 10), the extinction pattern on land is more consistent with volcanic sulfur aerosol-induced volcanic winters (4). Two small airfall ashes from lacustrine strata interbedded with CAMP lavas in the Newark and Hartford rift basins (**Fig. B**) in eastern North America provide evidence of such volcanic sulfur aerosols.

Modeling results of Landwehrs et al. (11) suggest that CAMP volcanic winters could overwhelm warming from CAMP pCO_2, producing large magnitude cooling (**Fig. C**). However, no direct proxy for volcanic sulfate exists and the injection mechanisms for the giant fissure eruptions are poorly constrained. Nonetheless, sulfur isotopic data from lacustrine strata suggest that CAMP eruptions did produce significant sulfur aerosols.





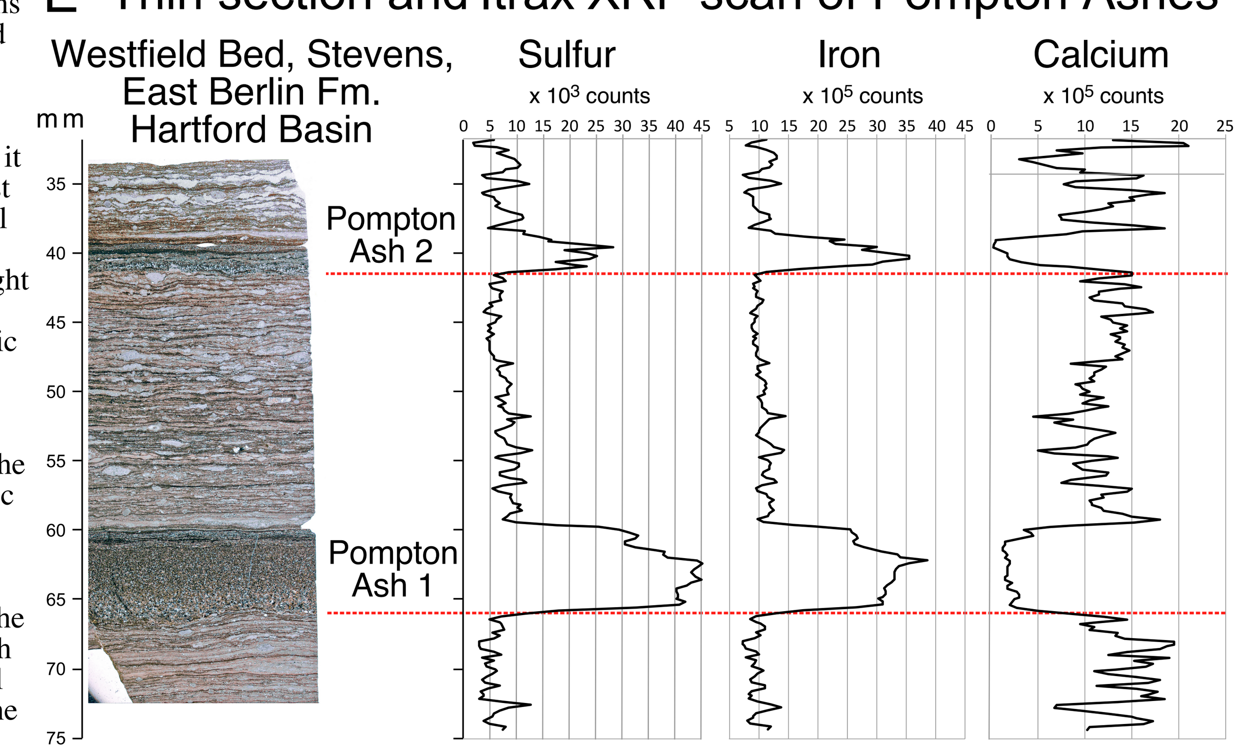
Pompton Ashes in the Towaco & East Berlin Formations

The two airfalls are called the Pompton Ashes and they occur in the middle Towaco Formation of the Newark Basin and the middle East Berlin Formation of the Hartford Basin (**Figs. C & D**). The ashes have been identified in 2 cores and at 1 outcrop in the Newark Basin (1, 2 and 3, **Fig. B**) and 2 cores and 5 outcrops (4, 5 and 6-10, **Fig. B**) in the Hartford Basin in these largely coeval, cyclical, orbitally-paced formations (3), exactly in the same position in correlative lacustrine cycles.

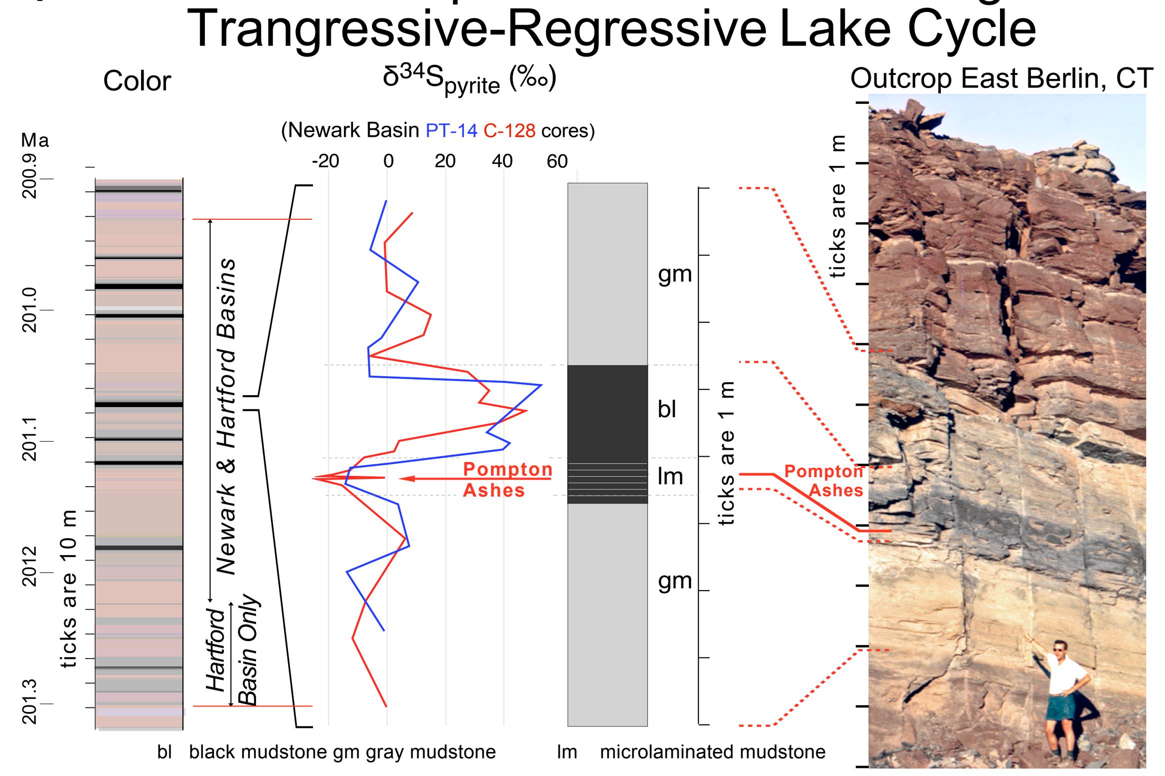
The ashes occur in dark-gray, deep-water, calcareous microlaminated mudstone with articulated fish and clam shrimp (**Fig. E**). The lower, Pompton Ash 1, is about 5 to 7 mm thick. It is graded, composed of sharply euhedral plagioclase laths in an originally glass matrix, with fine-grained feathery feldspars, carbonate, and sub-mm volcanic spherules of the same composition at its base (1, 12, 13). The upper is 1 to 2 mm thick and is similar to ash 1, but with smaller grain size. Both are overlain by a few thin laminae composed of what we interpret as recycled ash transported to the site with admixed non-volcanic sediment. Based on astrochronology (3) of the lacustrine strata and CA-ID-TIMS ages of the surrounding lavas (and their correlates) (8) the age of the ashes is about 201.05 Ma.

Both Pompton ashes tend to stand out in μ-XRF scans as excursions in S and Fe, inversely correlated to Ca (**Fig. E**). At this locality (Stevens, 6 in Fig. B), the Pompton Ash 1 is 16.7% pyrite by weight but at other localities it can be as low as 9.5% (e.g., East Berlin outcrop). In outcrop at all localities it has been found, Pompton Ash 1 weathers to bright orange mush which is almost certainly pigmented by a jarositic mineral from weathered pyrite and ash. There is no reason to think the high pyrite content is from the primary chemistry of the ash itself, but rather is diagenetic and post-depositional. Pompton Ash 2 does not weather as prominently and has a lower pyrite content based on XRF. The microlaminated matrix has much less pyrite averaging 2.7%, still high compared to most lacustrine strata.

E Thin section and Itrax XRF scan of Pompton Ashes

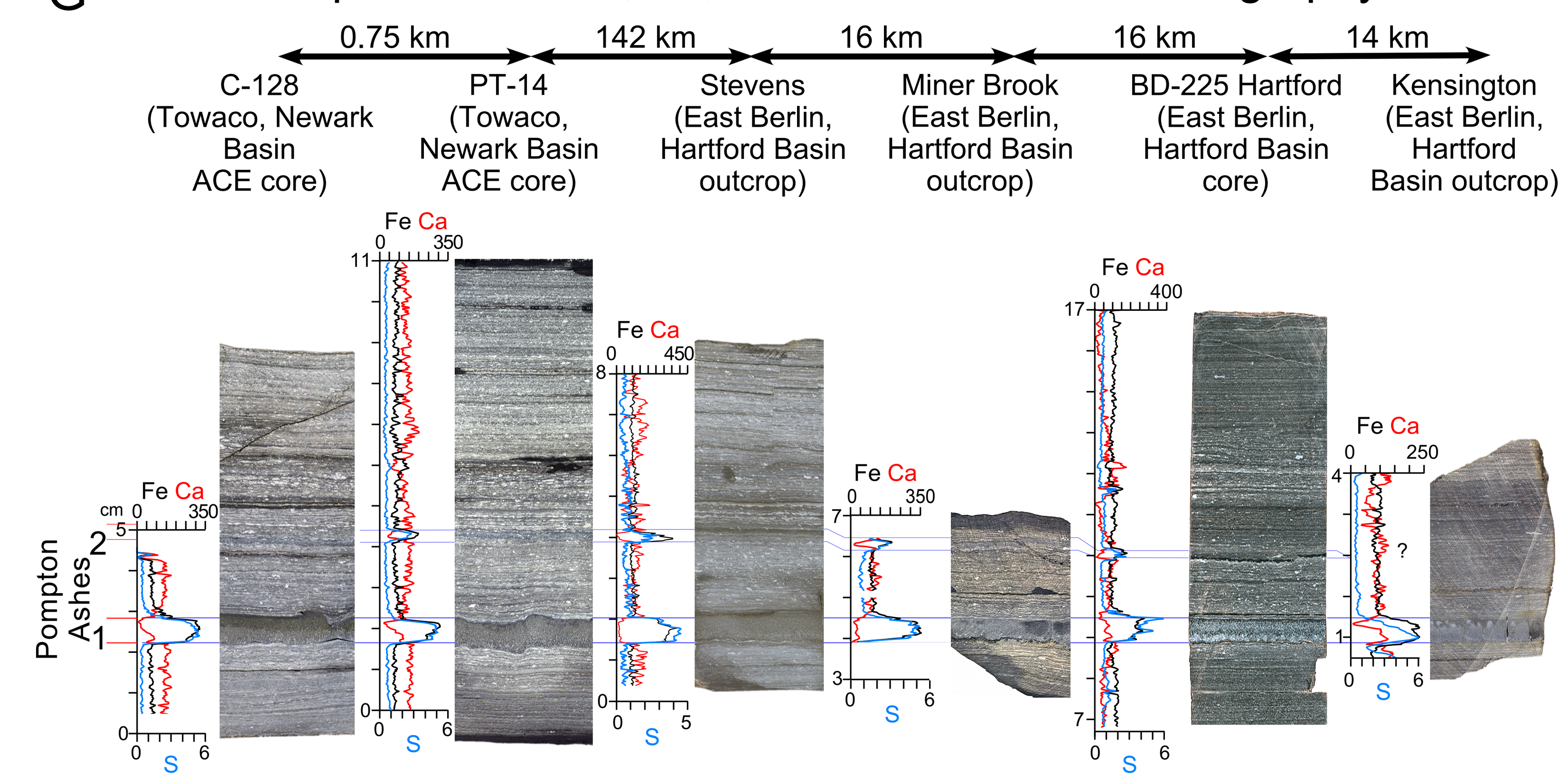


F Sulfur Isotopic Excursions in a Single Trangressive-Regressive Lake Cycle



Stüeken et al. (2) described $\delta^{34}S_{pyrite}$ variations in two Newark Basin cores with the Pompton Ashes (PT-14 and C128, Towaco Fm., Newark Basin: 1 and 2, respectively Fig. B). Average background $\delta^{34}S_{pyrite}$ hovers around 0‰ in gray, shallow-lake strata bracketing the black highstand bed. Most of the latter is characterized by a dramatic positive excursion in $\delta^{34}S_{pyrite}$ between +40‰ to +60‰, plausibly as a result of closed-system microbial sulfate reduction in a progressively ^{34}S-enriched reservoir. As this lake filled and reached its outlet during its early, hydrologically-open phase, $\delta^{34}S_{pyrite}$ in the basal microlaminated, fish-bearing basal layers of the highstand bed would be expected to remain around ~0‰. Instead, $\delta^{34}S_{pyrite}$ became more depleted than anywhere else in the cycle (-20‰), suggesting an input of sulfate into the lake that allowed greatly enhanced isotope discrimination.

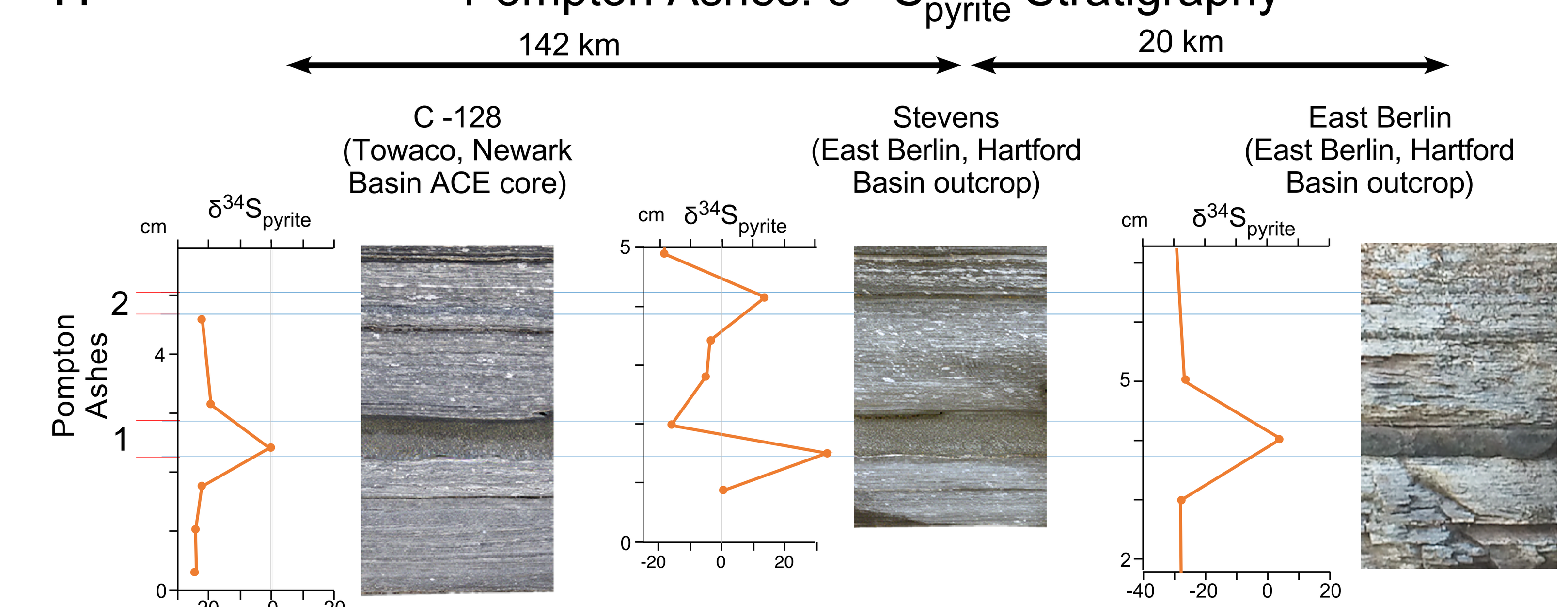
G Pompton Ashes: S, Fe, Ca Elemental XRF Stratigraphy



A surprising aspect of the Pompton Ashes is that they show no discernible thickness change over the 200 km over which they have been identified, and profiles of the ashes from slabs 142 km apart are similar at the sub-mm-scale (**Fig. G**). As ashes typically decrease in thickness rapidly and non-linearly (exponential, power law, Weibull) (15) away from their source the remarkably consistent thicknesses of the Pompton Ashes over 200 km, suggests that the source was both far away or very large, perhaps qualifying as super-eruptions. Although no other airfalls are known in these cyclical deposits at this time, they may not be recognizable in the bioturbated, rooted and well mixed shallow water strata that make up most of the section.

These are basaltic-andesitic ash chemically consistent with the CAMP (1, 12, 16). Pompton Ash 1 is characterized by a modest PGE anomaly with ~120 ppt Ir against a background of ~30 ppt and epsilon Nd values averaging -5.4 against a local background of -9.2 and a basin-scale background (Hartford) of -10.6. The REE pattern is indistinguishable from that of the Hampden, Hook Mt., and "recurrent" basalts (16).

H Pompton Ashes: $\delta^{34}S_{pyrite}$ Stratigraphy



For all three of the sites at which the Pompton Ashes have been sampled for $\delta^{34}S_{pyrite}$ in detail (**Fig. H**), Pompton Ash 1 has a strikingly more positive values $\delta^{34}S_{pyrite}$ (0 to 27‰) than the surrounding microlaminated mudstone which has $\delta^{34}S_{pyrite}$ values consistently more negative than -20‰. The more positive values of Pompton Ash 1 which also has very high concentration of diagenetic pyrite suggests closed system behavior within the pore space of the well after deposition. There is a suggestion that Pompton Ash 1 may have behaved similarly (Stevens locality). The strikingly negative excursion surrounding the Pompton Ashes, is consistent with direct inputs of volcanic aerosols from eruptions and subsequent drainage of airfall sulfur from the surrounding watershed that diffused into porewaters effecting the intervals a few centimeters above and below the ashes. This is similar to the Li et al. (17) in which similar magnitude negative $\delta^{34}S_{pyrite}$ excursions were used to infer input of sulfur aerosols from Siberian Trap eruptions at the end-Permian extinction.

The hypothesis that that the Pompton Ashes eruptions were associated with volcanic winters suggests that the major negative excursions in $\delta^{34}S_{pyrite}$ should be associated with $\delta^{18}O_{carbonate}$ values and $\Delta47_{carbonate}$ (carbonate clumped isotopes) results reflecting decreased temperatures. Further, pyrite in black mudstones in other cycles of the Towaco and East Berlin Formations lacking ashes should also lack negative $\delta^{34}S_{pyrite}$ excursions but should have the dramatic positive excursions.

References: **1**. P. E. Olsen *et al*., *Geological Society of America Abstracts with Programs* 48, doi: 10.1130/abs/2016NE-272509 (2016). **2**. E. E. Stüeken *et al*., *Geochimica et Cosmochimica Acta* 252, 240-267 (2019). **3**. P. E. Olsen *et al*., *PNAS* 116, 10664–10673 (2019). **4**. P. E. Olsen *et al*., *Science Advances* 8, eabo6342 (2022). **5**. A. Marzoli *et al*., *Science* 284, 616-618 (1999). **6**. M. R. Rampino, S. Self, in The Encyclopedia of Volcanoes, H. Sigurdsson, Ed. (Academic Press, Elsevier, Amsterdam, 2015), pp. 1049-1058. **7**. S. P. Hesselbo, S. A. Robinson, F. Surlyk, S. Piasecki, *Geology* 30, 251-254 (2002). **8**. T. J. Blackburn *et al*., *Science* 340, 941–945 (2013). **9**. C. P. Fox *et al*., *Geology* https://doi.org/10.1130/G49560.1 (2022). **10**. M. Trudgill *et al*., *5th EGU Galileo Conference: Mass extinctions, recovery and resilience*, 90 (2019). **11**. J. P. Landwehrs, G. Feulner, M. Hofmann, S. Petri, *Earth and Planetary Science Letters* 537 (2020). **12**. P. Olsen *et al*., *Goldschmidt Abstracts* 2019, 2511: https://goldschmidtabstracts.info/abstracts/abstractView?id=2019005267 (2019).
13. P. E. Olsen, A. Douglass, *A Field Trip for the International Ocean Discovery Program (IODP) Forum Meeting September 14-15, Palisades New York* ISBN: 978-0-942081-36-7, 1—44 (2022). **14**. J. Laskar, A. Fienga, M. Gastineau, H. Manche, *Astronomy and Astrophysics* 532, 1–15 (2011). **15**. C. Bonadonna *et al*., *JGR: Solid Earth* **116** (2011). **16**. P. E. Olsen *et al*., *Goldschmidt 2017 Abstracts*, https://goldschmidt.info/2017/abstracts/abstractView?id=2017006082 (2017).
17. M. Li *et al*., *Earth and Planetary Science Letters* **592**, 117634 (2022).