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Soil carbonate Δ_{47} paleotemperatures across the Paleocene-Eocene boundary: the Esplugafreda terrestrial record, Spain

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Massive additions of ^{13}C-depleted carbon to the atmosphere-ocean system at 55.9 Myr ago led to global warming of 5–8 °C, profound floral/faunal turnovers and alteration of the global hydrological cycle at the Paleocene-Eocene boundary. Climate and environmental changes over the late Paleocene and Paleocene-Eocene Thermal Maximum (PETM) are well-preserved in continental deposits, formed in the subtropical zone (paleolatitude ~35 °N), in the Tremp-Graus Basin, northern Spain. One of the key exposures is the Esplugafreda section, which is made up of ~250 m of red mudstones with abundant paleosols and contains numerous multi-episodic channel-like bodies of calcareous conglomerates and calcarenites. The paleosols contain abundant centimeter-sized soil nodules and gypsum indicating a semi-arid to arid paleoenvironment. The Paleocene-Eocene (P-E) boundary is located near the top of the continental section, based on a 6‰ negative carbon isotope excursion (CIE). The CIE spans more than 15–20 m of yellow cumulate paleosols formed during the Paleocene-Eocene Thermal Maximum (PETM). The post-PETM interval in the Esplugafreda section comprises 20 m of red paleosols rich in gypsum and characterized by normal soil nodule δ^{13}C values.

Here, we report the first carbonate clumped isotope thermometry data of selected soil carbonate bearing paleosol layers of the Esplugafreda sequence to quantify the magnitude of warming recorded in the sediments of this terrestrial subtropical site across the Paleocene-Eocene boundary. Soil nodules originated from red mudstone paleosols making up the upper part of the upper Paleocene Esplugafreda Formation and PETM yellow soils collected at two nearby sites. The nodules were sampled with a hand driller for Δ_{47} measurements, which were done using a Kiel IV carbonate device coupled to a Thermo Scientific 253 Plus IRMS at the Institute for Nuclear Research, Debrecen, Hungary. Stable carbon, oxygen isotope and clumped isotope compositions were calculated as the average of 8–16 replicate analyses of 100–150 µg of carbonate. The carbon

and oxygen isotope ratios are reported in δ notation in per mil (‰) relative to the Vienna Pee Dee Belemnite (VPDB), while the temperature-dependent mass 47 anomaly on the I-CDES$_{90°C}$ scale. Temperatures were calculated using the Kele et al. (2015) calibration modified by Bernasconi et al. (2018) and the Anderson et al. (2021) calibrations.

Soil carbonates of the Esplugafreda formation yield $\delta^{13}C_{carb}$ values between –8.55 and –5.85 ‰, while the PETM yellow soil carbonates are significantly more negative (–13.84 to –10.12 ‰), in good agreement with previous measurements. A much smaller, ~1.2 ‰ difference can be observed in the oxygen isotope compositions between these carbonates ($\delta^{18}O_{carb}$: –5.46 to –4.13 versus –6.35 to –4.47 ‰). The Δ_{47}-based paleotemperatures (T_{47carb}) indicate mean soil carbonate formation of 33.8±9.5 °C during the late Paleocene, which are close to modern summer temperatures of subtropical regions. By contrast, a much higher mean temperature was recorded by soil carbonates of the PETM yellow soils (39±8.5 °C) with extreme (>40 °C) temperatures occurring 4 times more frequently than over the late Paleocene.

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