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Evaluation of paleo-CO_2 proxy based on carbon isotope value of long chain *n*-alkanes and terpenoids from C_3 land plants

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Atmospheric CO_2 concentration affects the carbon isotope composition ($\delta^{13}C$) of plant tissue produced during photosynthesis. This observation has led to the suggestion that changes in the $\delta^{13}C$ value of bulk terrestrial organic matter (TOM) can be used to reconstruct past pCO_2 on geologic timescales. Bulk TOM, however, may be affected by degradation and source mixing, which can bias the $\delta^{13}C$ value, and therefore give systematically high or low estimates of pCO_2. Well-preserved long chain *n*-alkanes and terpenoids, representative of only higher-order land plants, are highly resistant to diagenesis and degradation, and may therefore provide a less-biased estimate of pCO_2 than bulk TOM. Here we show new pCO_2 estimates determined from published $\delta^{13}C$ data on long-chain odd-numbered *n*-alkanes and di- and tri-terpenoid extracted from early Paleogene samples. After correcting for changes in the $\delta^{13}C$ value of atmospheric CO_2, *n*-C_{27}, *n*-C_{29} and *n*-C_{31}, diterpenoid and triterpenoid show significantly higher discrimination during the early Paleogene compared to modern values, consistent with moderately high CO_2 levels during early Paleogene; *n*-C_{33}, showed no significant change in discrimination. These results support work based on bulk TOM showing increased discrimination and higher pCO_2 during the early Paleogene compared to today, and show the potential for the dominant long-chain *n*-alkanes and terpenoids to be used as a pCO_2 proxy.