## A 23 m.y. record of low atmospheric CO<sub>2</sub>

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In their recent paper, Cui et al. (2020) used a new iteration of their C<sub>3</sub> plant proxy to reconstruct  $pCO_2$  over the last 23 Ma. The initial version of this proxy used carbon isotope discrimination (D<sup>13</sup>C, calculated as the offset between the d<sup>13</sup>C of plant tissue [d<sup>13</sup>C<sub>p</sub>] and atmospheric CO<sub>2</sub> [d<sup>13</sup>C<sub>atm</sub>]) to estimate paleo-CO<sub>2</sub> (Schubert and Jahren, 2015), but recent work by different research groups has questioned the utility of this proxy (e.g., Kohn, 2016; Stein et al., in press). Previously, we used D<sup>13</sup>C data from *Arabidopsis thaliana* plants grown experimentally under different moisture and  $pCO_2$  conditions to show that this proxy is strongly impacted by variations in moisture availability and underpredicts  $pCO_2$  (Lomax et al., 2019). Here, we argue that the new version of the C<sub>3</sub> proxy presented by Cui et al. (2020), which is centered on d<sup>13</sup>C<sub>p</sub> rather than D<sup>13</sup>C, suffers from the same shortcomings. Therefore, it is unsuitable for addressing the core question posed in their paper, that is, how  $pCO_2$  levels in the geological past compare with those both in the present and predicted for the near future.

Using the new d<sup>13</sup>C<sub>p</sub> proxy to reconstruct *p*CO<sub>2</sub> from our existing *A. thaliana* data set (Jardine and Lomax, 2020; Lomax et al., 2019) shows that, like its predecessor, this proxy underestimates *p*CO<sub>2</sub> (Fig. 1A), although the effect is even more pronounced than previously (Fig. 1B). The proxy struggles to successfully predict *p*CO<sub>2</sub> for plants grown in >400 ppm conditions, which is particularly problematic because this is the core threshold for assessing whether past *p*CO<sub>2</sub> values exceed those of today. *p*CO<sub>2</sub> estimates are likely lower in this iteration of the proxy because rather than deriving a new relationship between d<sup>13</sup>C<sub>p</sub> and *p*CO<sub>2</sub>, Cui et al. (2020) used the model parameters (the A, B and C terms) from their D<sup>13</sup>C: *p*CO<sub>2</sub> curve (Schubert and Jahren, 2015). However, the d<sup>13</sup>C<sub>anomaly</sub> term of Cui et al. (2020; see their Equations 1 and 2) does not equal the D(D<sup>13</sup>C) term of Schubert and Jahren (2015; see their Equations 1 and 4) (Fig. 1C). The result is that *p*CO<sub>2</sub> predicted from d<sup>13</sup>C<sub>p</sub> is even lower than *p*CO<sub>2</sub> predicted from D<sup>13</sup>C, with the downward bias becoming particularly apparent at *p*CO<sub>2</sub> > 400 ppm (Fig. 1B).

As with the D<sup>13</sup>C version of the C<sub>3</sub> proxy, the new d<sup>13</sup>C-based proxy is impacted by moisture availability, especially at higher  $pCO_2$  levels (Fig. 1A). This is a critical issue in the timeseries presented by Cui et al. (2020), because hydrological changes are likely to have accompanied  $pCO_2$ -driven temperature changes, for instance across the mid-Miocene Climatic Optimum, ~17–14 Ma (Loughney et al., 2020). The extent to which the increase in  $pCO_2$  reconstructed for this time by Cui et al. (2020) (Fig. 1D) is due to increases in moisture availability cannot be evaluated with this proxy, nor can the impact of long-term continental drying through the late Neogene on the overall downward  $pCO_2$  trend.

Cui et al. (2020) used Monte Carlo resampling to quantify uncertainty in their  $pCO_2$  reconstruction, and presented these uncertainties via a LOWESS smoother with a 68% confidence interval. A 68% confidence interval represents an abnormally low level of statistical confidence, and is too narrow to robustly determine whether  $pCO_2$  values in the past exclude today's levels or those of the future. Plotting 95% confidence intervals (and therefore utilizing the usual a = 0.05 level for statistical inference) shows that  $pCO_2$  values of >500 ppm are entirely consistent with Cui et al.'s reconstruction for much of the last 23 Ma, including in the Pliocene and Pleistocene. The C<sub>3</sub> proxy therefore fails to reject elevated  $pCO_2$  conditions for the late Neogene and Quaternary, despite the downward biasing in the  $pCO_2$  estimates themselves (Fig. 1D).

Understanding the relationship between  $pCO_2$  and global climate is vital for forecasting the response of the climate system to anthropogenic  $CO_2$  emissions. As such,  $pCO_2$  proxies are essential, but they need to be robust and thoroughly validated. Terrestrial fossil organic carbon may be ubiquitous in sediments, but because of impact of moisture availability on  $d^{13}C_p$ , and the inadequately derived relationship between  $d^{13}C_p$  and  $pCO_2$  used by Cui et al. (2020), we maintain (Lomax et al., 2019) that the C<sub>3</sub> proxy is not suitable for reconstructing  $pCO_2$  in the geological past.

## **REFERENCES CITED**

- Cui, Y., Schubert, B.A., and Jahren, A.H., 2020, A 23 m.y. record of low atmospheric CO<sub>2</sub>: Geology, v. 48, p. 888–892, <u>https://doi.org/10.1130/G47681.1</u>.
- Jardine, P. E., and Lomax, B. H., 2020 Data and code for "A 23 m.y. record of low atmospheric CO<sub>2</sub>: Comment: Geology, v. 48, p.": Figshare, https://doi .org/10.6084/m9.figshare.13194554
- Kohn, M.J., 2016, Carbon isotope discrimination in C<sub>3</sub> land plants is independent of natural variations in *p*CO<sub>2</sub>: Geochemical Perspectives Letters, v. 2, p. 35–43, <u>https://doi.org/10.7185/geochemlet.1604</u>.
- Lomax, B.H., Lake, J.A., Leng, M.J., and Jardine, P.E., 2019, An experimental evaluation of the use of D<sup>13</sup>C as a proxy for palaeoatmospheric CO<sub>2</sub>: Geochimica et Cosmochimica Acta, v. 247, p. 162–174, https://doi.org/10.1016/j.gca.2018.12.026.
- Loughney, K.M., Hren, M.T., Smith, S.Y., and Pappas, J.L., 2020, Vegetation and habitat change in southern California through the Middle Miocene Climatic Optimum: Paleoenvironmental records from the Barstow Formation, Mojave Desert, USA: Geological Society of America Bulletin, v. 132, p. 113–129, <u>https://doi.org/10.1130/B35061.1</u>.
- Schubert, B.A., and Jahren, A.H., 2015, Global increase in plant carbon isotope fractionation following the Last Glacial Maximum caused by increase in atmospheric *p*CO<sub>2</sub>: Geology, v. 43, p. 435–438, <u>https://doi.org/10.1130</u>
  - <u>/G36467.1</u>.
- Stein, R.A., Sheldon, N.D., and Smith, S.Y., C<sub>3</sub> plant carbon isotope discrimination does not respond to CO<sub>2</sub> concentration on decadal to centennial timescales: The New Phytologist, https://doi.org/10.1111/nph.17030 (in press)



 $\frac{1}{2}$  J using the d<sup>13</sup>C<sub>p</sub>-based C<sub>3</sub> proxy  $\Rightarrow$  data set of Lomax et al. (2019).

Points are colored by water treatment. (B) Comparison of estimated  $pCO_2$  using the D<sup>13</sup>C-based C<sub>3</sub> proxy of Schubert and Jahren (2015) and the d<sup>13</sup>C<sub>p</sub>-based C<sub>3</sub> proxy of Cui et al. (2020). (C) Comparison of the D(D<sup>13</sup>C) term of Schubert and Jahren (2015) and the d<sup>13</sup>C<sub>anomaly</sub> term of Cui et al. (2020). (D) The time series presented by Cui et al. (2020), based on their d<sup>13</sup>C<sub>p</sub>-based C<sub>3</sub> proxy, with a LOESS smoother and both 68% and 95% confidence intervals.