



*Paleoceanography and Paleoclimatology*

Supporting Information for

## **Hydrologic change in New Zealand during the last deglaciation linked to reorganization of the Southern Hemisphere westerly winds**

Jessica L. Hinojosa<sup>1\*</sup>, Christopher M. Moy<sup>2</sup>, Marcus Vandergoes<sup>3</sup>, Sarah J. Feakins<sup>4</sup>, and Alex L. Sessions<sup>1</sup>

<sup>1</sup> Division of Geological and Planetary Sciences, California Institute of Technology. 1200 E. California Blvd. MC 100-23, Pasadena, CA 91125

<sup>2</sup> Department of Geology, University of Otago. PO Box 56, Department of Geology, University of Otago, Dunedin, New Zealand 9054

<sup>3</sup> Department of Paleontology & Environmental Change, GNS Science. PO Box 30-368, Lower Hutt, New Zealand 5040

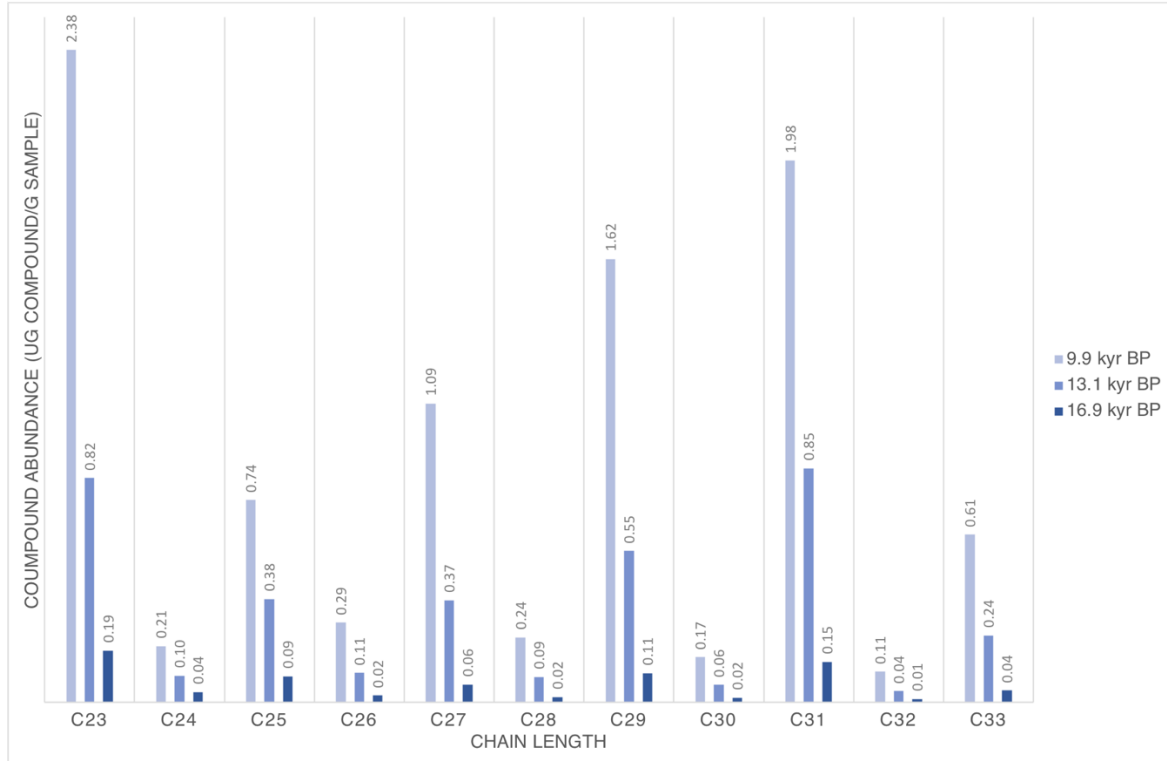
<sup>4</sup> Department of Earth Sciences, University of Southern California. Los Angeles, CA 90089

### **Contents of this file**

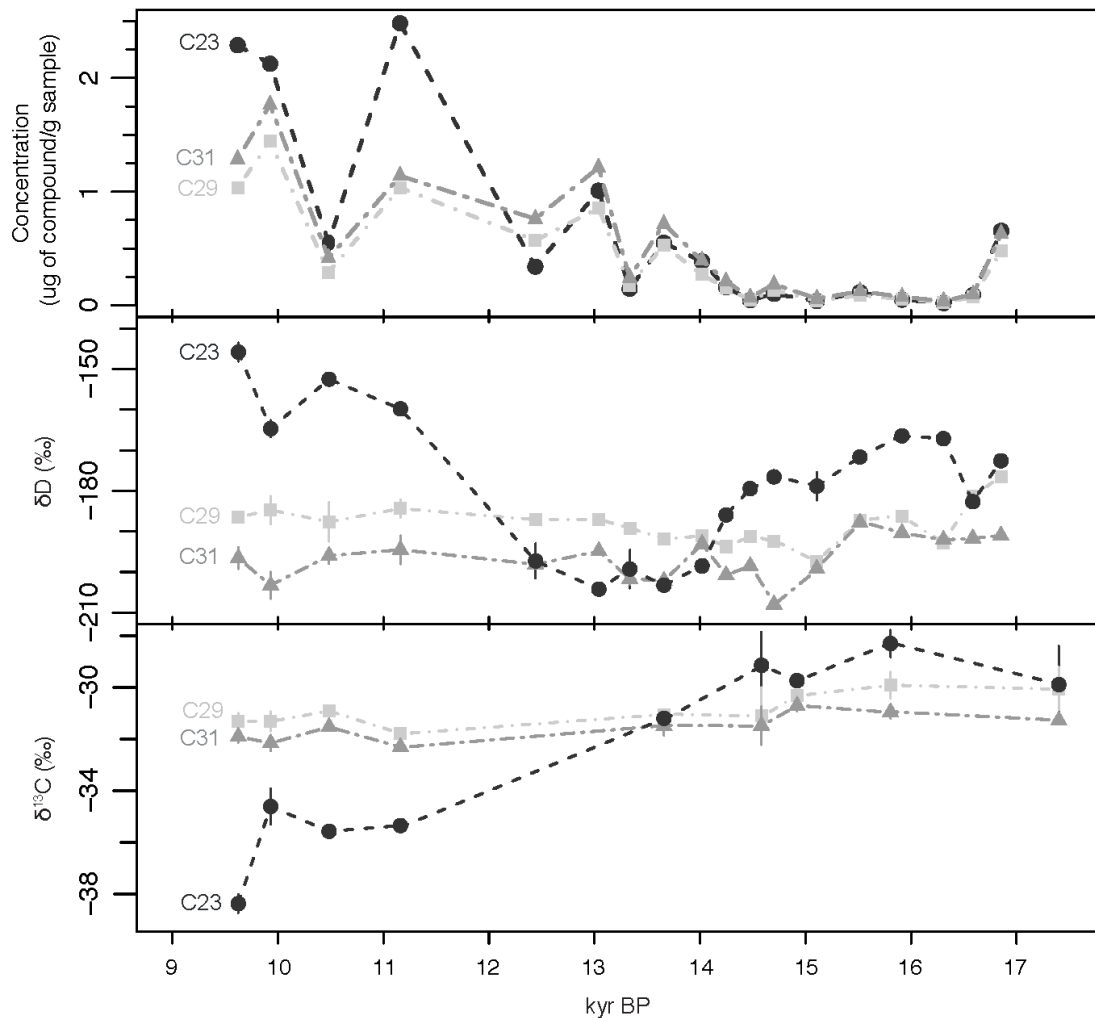
Figures S1, S2, and S3; Table S1; Discussion

### **Introduction**

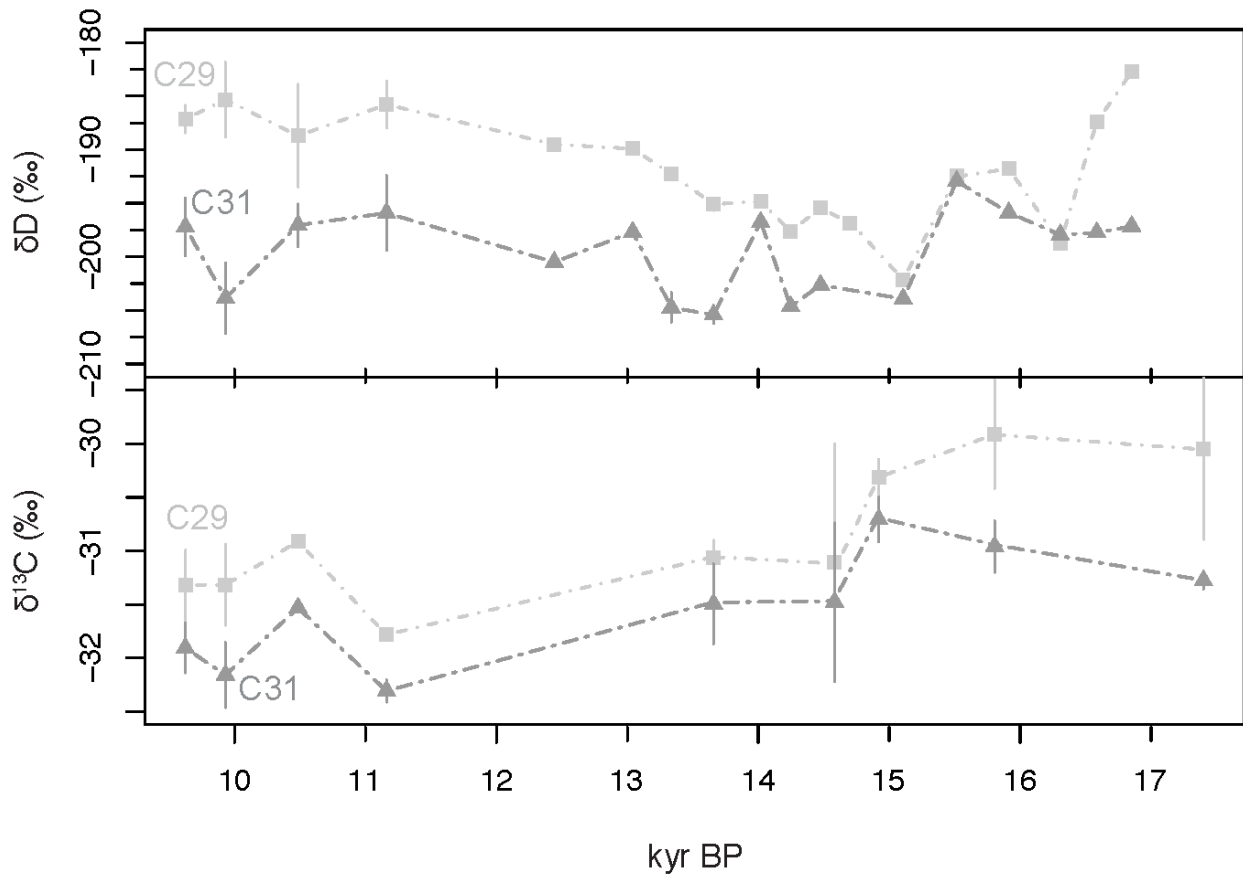
We present two supplementary figures and an extended discussion regarding the n-alkane proxy system used within this manuscript. Figure S1 is a comparison of n-alkane chain lengths at three different time slices within the data, showing a strong bimodality in chain length distribution. Figure S2 compares H and C stable isotopes between the mid-chain (C23) and long-chain (C29 and C31) n-alkanes in this record. Table S1 includes additional information on n-alkane distributions and key parameters like average chain length (ACL).



**Figure S1.** Relative abundances of mid- and long-chain n-alkanes from three representative samples throughout the Lake Hayes sedimentary record. There is a clear odd-over-even preference, as well as a bimodality, with peaks in C23 (often associated with aquatic macrophytes) [Ficken *et al.*, 2000] and C29 and C31 (often associated with terrestrial plant waxes) [Eglinton and Hamilton, 1967; Eglinton and Eglinton, 2008].



**Figure S2.** Top: Relative abundances of C23, C29, and C31 in the Lake Hayes sediment core. Middle:  $\delta D$  by compound. Bottom:  $\delta^{13}C$  by compound, measured at fewer points than  $\delta D$ . In middle and bottom panels, error bars represent 1 SD of replicate analyses per sample. Samples with no error bars did not have enough material for replicate runs.



**Figure S3.** Same as two lower panels above, but just for long-chain n-alkanes (C29, light gray squares and C31, dark gray triangles).

Age (wt. avg)	CPI (C <sub>25</sub> -C <sub>33</sub> ) (after Schefuss et al. 2003)	ACL (C <sub>25</sub> -C <sub>33</sub> )
9625	3.90	29.3
9932	3.81	29.2
9987	3.73	29.1
10486	2.88	29.1
11162	3.20	28.9
11223	3.59	29.0
12001	3.49	29.5
12443	4.56	29.4
13059	3.52	29.3
13155	3.99	29.2
13336	4.29	29.4
13745	3.75	29.3
14015	3.08	29.1
14245	3.03	29.1
14474	2.51	29.1
14700	2.68	29.3
15105	2.38	29.3
15319	2.14	29.0
15516	2.37	29.1
15750	2.67	29.0
15914	2.61	29.2
16307	2.29	29.5
16585	2.75	29.1
16728	2.38	29.4
16857	2.03	28.6
16935	3.17	28.9
17140	4.44	29.8
17494	2.87	29.7

**Table S1.** Carbon preference index (CPI) [Schefuß et al., 2003] and average chain length (ACL) for the Lake Hayes sediment core.

#### **Discussion of n-alkane distributions and isotopes**

The Lake Hayes record shows significantly divergent trends between the C<sub>23</sub> n-alkane and the C<sub>29</sub> and C<sub>31</sub> n-alkanes. The latter two covary significantly and are likely representative of a terrestrial plant source. The use of H isotopes in the C<sub>23</sub> n-alkane archive has been applied to reconstruct changes in lake isotopic composition [Sauer et al., 2001; Huang et al., 2004;

Sachse *et al.*, 2004], but also has been shown to correlate better to annual precipitation at certain high-latitude sites [McFarlin *et al.*, 2019].

In the Lake Hayes record, despite lacking modern calibration data, we link the  $\delta D_{C23}$  to lake isotopic composition rather than annual precipitation due to the disconnect between  $\delta D_{C23}$  and  $\delta D_{\text{long-chain}}$ . However, this link relies on the assumption that  $\delta D_{\text{long-chain}}$  is a faithful recorder of precipitation trends through the deglacial record, independent of water use efficiency changes and/or vegetation shifts. We attempt to address the latter by looking at the  $\delta^{13}C_{\text{long-chain}}$  (Fig. S2), which does not undergo significant shifts in association with the major climatic intervals (HS1, ACR, YD, early Holocene), although there might be a long-term shift toward more negative  $\delta^{13}C$  for each n-alkane with time.

To assess changes in water use efficiency, we can look at the  $\delta D_{\text{long-chain}}$  during intervals of interpreted drier conditions. During these intervals, we would expect transpiration to increase, and D-enrichment to occur [Feakins and Sessions, 2010]. Indeed, there is a positive shift in the  $\delta D_{C29}$  from  $\sim 202\text{‰}$  at 15.1 ka to  $-187\text{‰}$  at 9.6 ka, but the trend is not as pronounced for  $\delta D_{C29}$ . Thus, although there is possible influence of water-use efficiency affecting  $\delta D_{\text{long-chain}}$ , we interpret this trend to reflect average precipitation over time.

The much larger isotopic shifts seen in the C23 records are likely to reflect changes within Lake Hayes, but again, some confounding influences cannot be ruled out. The most important and difficult to constrain is the source of the C23. While the C23 n-alkane is often attributed to aquatic macrophytes [Ficken *et al.*, 2000], emergent and terrestrial plants can contain up to 20 times the lipid concentration of submerged species [Aichner *et al.*, 2010], thus terrestrial input of C23 may influence the  $\delta D_{C23}$  record. However, if that were the case, it would be more likely that the  $\delta D_{C23}$  would converge with the  $\delta D_{\text{long-chain}}$ , rather than the strong decoupling that is recorded.

A remaining unknown is the cause of the large  $\delta^{13}C_{C23}$  shift seen in the early Holocene (9‰ depletion relative to 14.5 ka; Fig. S2). Because we invoke significant changes in carbonate chemistry of the lake from the YD to early Holocene, we must also consider the effect of changing alkalinity and pH on primary producers. Aichner *et al.* [2010] nicely discuss the expected compound-specific  $\delta^{13}C$  offset for macrophytes that are able to assimilate  $\text{HCO}_3^-$  versus dissolved  $\text{CO}_2$ . Because the  $\delta^{13}C$  value of  $\text{HCO}_3^-$  is  $\sim 10\text{‰}$  higher than dissolved  $\text{CO}_2$  [Mook *et al.*, 1974], species that can assimilate the former are likely to be more  $^{13}C$  enriched. This could have been the case for aquatic macrophytes during the YD, especially during the Ca/Ti peak associated with high alkalinity and endogenic carbonate production in Lake Hayes. A decrease in alkalinity in the lake and a return to dissolved  $\text{CO}_2$  utilization could then account for some, if not all, of the large  $\delta^{13}C_{C23}$  shift seen in the early Holocene.

## References

- Aichner, B., U. Herzschuh, and H. Wilkes (2010), Influence of aquatic macrophytes on the stable carbon isotopic signatures of sedimentary organic matter in lakes on the Tibetan Plateau, *Organic Geochemistry*, 41(7), 706–718, doi:10.1016/j.orggeochem.2010.02.002.
- Eglinton, G., and R. J. Hamilton (1967), Leaf Epicuticular Waxes, *Science*, 156(3780), 1322–1335, doi:10.1126/science.156.3780.1322.
- Eglinton, T. I., and G. Eglinton (2008), Molecular proxies for paleoclimatology, *EPSL*, 275(1-2), 1–16, doi:10.1016/j.epsl.2008.07.012.

- Feakins, S. J., and A. L. Sessions (2010), Controls on the D/H ratios of plant leaf waxes in an arid ecosystem, *GCA*, 74(7), 2128–2141, doi:10.1016/j.gca.2010.01.016.
- Ficken, K. J., B. Li, D. L. Swain, and G. Eglinton (2000), An n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes, *Organic Geochemistry*, 31(7-8), 745–749, doi:10.1016/S0146-6380(00)00081-4.
- Huang, Y., B. Shuman, Y. Wang, and T. Webb (2004), Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test, *J Paleolimnol*, 31(3), 363–375, doi:10.1023/B:JOPL.0000021855.80535.13.
- McFarlin, J. M., Y. Axford, A. L. Masterson, and M. R. Osburn (2019), Calibration of modern sedimentary d2H plant wax-water relationships in Greenland lakes, *QSR*, 225, 105978, doi:10.1016/j.quascirev.2019.105978.
- Mook, W. G., J. C. Bommerson, and W. H. Staverman (1974), Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide, *EPSL*, 22(2), 169–176, doi:10.1016/0012-821X(74)90078-8.
- Sachse, D., J. Radke, and G. Gleixner (2004), Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability, *GCA*, 68(23), 4877–4889, doi:10.1016/j.gca.2004.06.004.
- Sauer, P. E., T. I. Eglinton, J. M. Hayes, A. Schimmelman, and A. L. Sessions (2001), Compound-specific D/H ratios of lipid biomarkers from sediments as a proxy for environmental and climatic conditions, *GCA*, 65(2), 213–222.
- Schefuß, E., V. Ratmeyer, J.-B. W. Stuut, J. H. F. Jansen, and J. S. Sinninghe Damsté (2003), Carbon isotope analyses of n-alkanes in dust from the lower atmosphere over the central eastern Atlantic, *GCA*, 67(10), 1757–1767, doi:10.1016/S0016-7037(02)01414-X.