

# Supporting Information for “Deep heat: proxies, Miocene ice, and an end in sight for paleoclimate paradoxes?”

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1. Text S1 to S2

## Text S1. Derivation of main text Fig. 1.

Analytical reproducibility:

1.  $\delta^{18}\text{O}$ . Long term reproducibility of NBS-19 is typically 0.07‰; using an approximate relationship between  $\delta^{18}\text{O}$  and temperature of 0.23‰/1°C gives  $\pm 0.28^\circ\text{C}$  [Marchitto *et al.*, 2014].
2. Mg/Ca. Analytical reproducibility is typically better than 3%; using an approximate relationship between Mg/Ca and temperature of 5%/1°C gives  $\pm 0.60^\circ\text{C}$  [Lear *et al.*, 2010].
3. Mg/Li. Long-term Li/Ca precision is  $\sim 2\%$ ; using a linear Mg/Li-temperature slope of 0.0124, percent error depends on the absolute Mg/Li value, ranging between 0.21-0.43 °C at temperatures of 5-20°C [Bryan & Marchitto, 2010].
4.  $\Delta_{47}$ . Analytical-derived uncertainty depends on how replicate measurements are pooled [see Modestou *et al.*, 2020]. A typical uncertainty from their Fig. 4f is  $\pm 3.1^\circ\text{C}$ .

The carbonate system:

1.  $\delta^{18}\text{O}$ . Uchikawa & Zeebe, [2010] report a slope of  $-0.89$  between  $\delta^{18}\text{O}$  and pH in a planktonic foraminifer species. Given a Neogene pH range of between  $+0.15$  to  $-0.3$  units relative to today [Sosdian *et al.*, 2018], this equates to a temperature bias of  $+0.73$  to  $-1.47^\circ\text{C}$  based on the above relationship between  $\delta^{18}\text{O}$  and temperature. Note that the pH effect present in planktonic foraminifera has so far not been found in benthic species such that this source of uncertainty remains hypothetical [Marchitto *et al.*, 2014].
2. Mg/Ca. Using a Mg/Ca- $[\text{CO}_3^{2-}]$  slope of 0.0086, a possible  $[\text{CO}_3^{2-}]$  variation of  $\pm 40 \mu\text{mol/mol}$  [Lear *et al.*, 2010; Yu *et al.*, 2013], and the above relationship between Mg/Ca and temperature, the possible temperature bias is  $+3.17$  to  $-3.77^\circ\text{C}$  [Lear *et al.*, 2010; 2015].
3. Mg/Li. As this proxy aims to account for  $\Delta[\text{CO}_3^{2-}]$ , no bias is assumed.
4.  $\Delta_{47}$ . No carbonate system control has been identified over the range that these parameters are likely to have varied over the Cenozoic [Tripathi *et al.*, 2015].

Seawater elemental or isotopic chemistry:

1.  $\delta^{18}\text{O}$ . Assuming seawater  $\delta^{18}\text{O}$  can vary between  $-1\%$  VSMOW (ice free) and  $+1\%$  (LGM conditions) in the deep ocean, this equates to a temperature bias of  $\pm 4.55^\circ\text{C}$  based on the above relationship between  $\delta^{18}\text{O}$  and temperature.
2. Mg/Ca. Using a power seawater-shell Mg/Ca relationship with a coefficient of 0.52 [Evans & Müller, 2012], and considering that the seawater Mg/Ca ratio in the Neogene was up to 2 mol/mol lower than today (but never higher than at present) [Evans *et al.*, 2018], Mg/Ca-derived temperatures could be up to  $5.01^\circ\text{C}$  too cool based on the above relationship between Mg/Ca and temperature.
3. Mg/Li. The effect of changing seawater chemistry on Mg/Li is difficult to determine because little is known about the secular evolution of the seawater Mg/Li ratio. If [Li] remained constant, and Neogene seawater [Mg] was up to 20% lower than at present [Brennan *et al.*, 2013], then Mg/Li could be biased on the order of  $\sim 1\text{-}2^\circ\text{C}$ , although this remains to be determined.
4.  $\Delta_{47}$ . No seawater chemistry control has been identified.

**Text S2. Recalculation of Mg/Ca SST shown in main text Fig. 2.**

Mg/Ca data from Shevenell *et al.* [2004] were recalculated using the *Globigerina bulloides* equation of Gray & Evans [2019], which accounts for changes in pH. Middle Miocene pH was taken from Sosdian *et al.* [2018], with linear interpolation between the data reported in that study. Because seawater Mg/Ca was lower than modern in the Miocene [Evans *et al.*, 2018], the constant term of the calibration equation was modified to account for this, by multiplying by  $3.5^{0.64}/5.2^{0.64}$ , where 3.5 and 5.2 are the Miocene and modern seawater Mg/Ca ratios respectively, and 0.64 is an estimate of the power coefficient of the seawater-calcite Mg/Ca relationship based on a compilation of several calibrated species as well as inorganic calcite [Mucci & Morse, 1983; Evans *et al.*, 2015; 2016; Holland *et al.*, 2020].

**References**

- Brennan, S.T., Lowenstein, T.K. and Cendón, D.I., 2013. The major-ion composition of Cenozoic seawater: The past 36 million years from fluid inclusions in marine halite. *American Journal of Science*, 313: 713-775.
- Bryan, S., Marchitto, T., 2008. Mg/Ca-temperature proxy in benthic foraminifera: New calibrations from the Florida Straits and a hypothesis regarding Mg/Li. *Paleoceanography*, 23: doi:10.1029/2007PA001553.
- Evans, D. and Müller, W., 2012. Deep time foraminifera Mg/Ca paleothermometry: Nonlinear correction for secular change in seawater Mg/Ca. *Paleoceanography*, 27: doi.org/10.1029/2012PA002315.
- Evans, D., Erez, J., Oron, S. and Müller, W., 2015. Mg/Ca-temperature and seawater-test chemistry relationships in the shallow-dwelling large benthic foraminifera *Operculina ammonoides*. *Geochimica et Cosmochimica Acta*, 148: 325-342.
- Evans, D., Brierley, C., Raymo, M.E., Erez, J. and Müller, W., 2016. Planktic foraminifera shell chemistry response to seawater chemistry: Pliocene-Pleistocene seawater Mg/Ca, temperature and sea level change. *Earth and Planetary Science Letters*, 438: 139-148.
- Evans, D., Sahoo, N., Renema, W., Cotton, L.J., Müller, W., Todd, J.A., Saraswati, P.K., Stassen, P., Ziegler, M., Pearson, P.N. and Valdes, P.J., 2018. Eocene greenhouse climate revealed by coupled clumped isotope-Mg/Ca thermometry. *Proceedings of the National Academy of Sciences*, 115: 1174-1179.
- Gray, W.R. and Evans, D., 2019. Nonthermal influences on Mg/Ca in planktonic foraminifera: a review of culture studies and application to the Last Glacial Maximum. *Paleoceanography and Paleoclimatology*, 34: 306-315.
- Holland, K., Branson, O., Haynes, L.L., Hönisch, B., Allen, K.A., Russell, A.D., Fehrenbacher, J.S., Spero, H.J. and Eggins, S.M., 2020. Constraining multiple controls on planktic foraminifera Mg/Ca. *Geochimica et Cosmochimica Acta*, 273: 116-136.
- Lear, C.H., Mawbey, E.M. and Rosenthal, Y., 2010. Cenozoic benthic foraminiferal Mg/Ca and Li/Ca records: Toward unlocking temperatures and saturation states. *Paleoceanography*, 25: doi.org/10.1029/2009PA001880.
- Lear, C.H., Coxall, H.K., Foster, G.L., Lunt, D.J., Mawbey, E.M., Rosenthal, Y., Sosdian, S.M., Thomas, E. and Wilson, P.A., 2015. Neogene ice volume and ocean temperatures: Insights from infaunal foraminiferal Mg/Ca paleothermometry. *Paleoceanography*, 30: 1437-1454.
- Marchitto, T. M., W. B. Curry, J. Lynch-Stieglitz, S. P. Bryan, K. M. Cobb, and D. C. Lund. 2014. Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera. *Geochimica et Cosmochimica Acta* 130: 1-11.
- Modestou, S.E., Leutert, T.J., Fernandez, A., Lear, C.H. and Meckler, A.N., Warm middle Miocene Indian Ocean bottom water temperatures: comparison of clumped isotope and Mg/Ca based estimates. *Paleoceanography and Paleoclimatology*, 35: doi.org/10.1029/2020PA003927.
- Mucci, A. and Morse, J.W., 1983. The incorporation of Mg<sup>2+</sup> and Sr<sup>2+</sup> into calcite overgrowths: influences of growth rate and solution composition. *Geochimica et Cosmochimica Acta*, 47: 217-233.
- Shevenell, A.E., Kennett, J.P. and Lea, D.W., 2004. Middle Miocene southern ocean cooling and Antarctic cryosphere expansion. *Science*, 305: 1766-1770.
- Tripati, A.K., Hill, P.S., Eagle, R.A., Mosenfelder, J.L., Tang, J., Schauble, E.A., Eiler, J.M., Zeebe, R.E., Uchikawa, J., Coplen, T.B. and Ries, J.B., 2015. Beyond temperature: Clumped isotope signatures in dissolved inorganic carbon species and the influence of solution chemistry on carbonate mineral composition. *Geochimica et Cosmochimica Acta*, 166: 344-371.
- Uchikawa, J. and Zeebe, R.E., 2010. Examining possible effects of seawater pH decline on foraminiferal stable isotopes during the Paleocene-Eocene Thermal Maximum. *Paleoceanography*, 25: doi.org/10.1029/2009PA001864.
- Yu, J., Anderson, R., Jin, Z., Rae, J., Opdyke, B., Eggins, S., 2013. Responses of the deep ocean carbonate system to carbon reorganization during the Last Glacial-interglacial cycle. *Quaternary Science Reviews*, 76: 39.