Ring Index: Towards quality-controls for the TEX$_{86}$ paleothermometer

YI GE ZHANG[*] AND MARK PAGANI

Department of Geology and Geophysics, Yale University, New Haven, CT 06511, yige.zhang@yale.edu (*presenting author)

The ocean temperature proxy TEX$_{86}$ is founded on the distribution of cyclopentane rings associated with the archaeal membrane lipids, glycerol dialkyl glycerol tetraethers (GDGTs). Because GDGTs are ubiquitous in marine sediments, TEX$_{86}$ temperatures have been increasingly applied to a variety of marine settings from the Cretaceous through the Cenozoic. However, some TEX$_{86}$-derived paleotemperatures are known to substantially deviate from other proxy-based temeprature records, and appear to challenge our physical understanding of the climate system. These issues could be due, in part, to incomplete knowledge of GDGT production, transportation and preservation, or evolutionary effects that cause the TEX$_{86}$ temperature calibration to deviate from modern relationships. Presently, there is no established criteria to determine the quality or veracity of TEX$_{86}$ paleotemperatures.

Here we report a potential method to assess the veracity of TEX$_{86}$ temperatures using the close relationship between Ring Index (RI, weighted average number of cyclopentane rings in GDGTs) and TEX$_{86}$ in the modern ocean, computed from surface sediment dataset published by Kim et al., (2010) and Ho et al., (2011) [1, 2]. Correlation between RI and TEX$_{86}$ is no surprise because TEX$_{86}$ is based on the observation that the average number of cyclopentane rings in the GDGT pool increases with growth temperature [3]. In other words, RI and TEX$_{86}$ will always closely correlate if the GDGT distribution is temperature dependent, although RI represents the total weighted ring average while TEX$_{86}$ represents a subset of GDGTs using four compounds. When RI and TEX$_{86}$ values are decoupled, it suggests that environmental signals other than temperature influence the relative adundance of GDGTs. Indeed, the modern ocean RI-TEX$_{86}$ correlation disappears from samples associated with gas hydrates where GDGTs are derived from methanotrophic archaea [4]. Alternatively, when RI and TEX$_{86}$ are related but their relationship deviates from the correlation expressed by modern ocean GDGT distribution, it likely implies that TEX$_{86}$ is still reflecting temperature, but application of the modern calibration is no longer warranted and the precision of the TEX$_{86}$ temperature is compromised.

We evaluated the RI-TEX$_{86}$ relationship using published and unpublished data from the Cretaceous to Cenozoic and demonstrate that in sample sets where the RI-TEX$_{86}$ relationship resembles the modern calibration, TEX$_{86}$ appears to produce temperature estimates that are more consistent, and in better agreements with other temperature proxies. In contrast, TEX$_{86}$-derived temperatures often lack consistency and are less comparable to other available temperature proxies (e.g. U$^{k'}_{37}$, Mg/Ca) when the modern RI-TEX$_{86}$ correlation fails.

[1] Kim et al., (2010) *Geochim. Cosmochim. Acta* **74**, 4639-4654.
[2] Ho et al., (2011) *Org. Geochem.* **42**, 94-99.
[3] Schouten et al., (2002) *Earth Planet. Sci. Lett.* **204**, 265-274.
[4] Zhang et al., (2011) *Earth Planet. Sci. Lett.* **307**, 525-534.

Light Elements in the Core and Equilibration Degree with Silicate Mantle: Perspective from First-Principles Molecular Dynamics

YIGANG ZHANG[1], QING-ZHU YIN[2*]

[1]Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China, zhangyg@mail.iggcas.ac.cn
[2]Department of Geology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA (*presenting author) qyin@ucdavis.edu

The degree of chemical equilibration (hereafter as *Ke*), defined as the cumulative mass fraction of the metalic core in equilibrium with the silicate mantle during the Earth accretion processes, greatly influences determination of the timing of the Earth core formation [1]. If *Ke* is larger than ~0.4, Hf-W chronology implies a fast accretion in less than 30 Myr for the Earth. Otherwise, Hf-W data can only be used to constrain the *Ke* instead of timing [1]. Here we use the two-phase first-principles molecular dynamics (FPMD) [2] to constrain the solubility of light elements in liquid iron in equilibration with silicate melt at temperatures from 2500 to 4200 K, pressures from 20 to 120 GPa, and two compositions simplified from the "O-bearing" and "Si-bearing" bulk Earth model compositions of McDonough [3]. The solubility data are then used in the simulations of the many possible accretion scenarios of the Earth as outlined in [4], considering magma ocean depth, homogeneous vs heterogeneous accretion etc. For each accretion route, we calculate the effective core-mantle equilibration degree (*Ke*),

$$K_e = \sum_i^N Ke_i \times W_i$$

where *Ke$_i$ and W$_i$* are the core-mantle equilibration degree and the accreted mass fraction of the ith step, respectively. The successful *Ke* are selected based on the criterion that the resulting Earth's core must meet the required density deficit [5]. The *Ke* in those successful simulations are all found to be larger than 0.57, implying that the core-mantle differentiation has to occur early [1], within 30 millions years from the beginning of the solar system as originally stated [6].

Additional simulations (all at 3200 K and 40 GPa) are also made to calculate the partition coefficients of several other light elements. Combined with the bulk Earth compositions of these elements [3], it is found Si, O, and S are the major light elements in the core while C, P, Mg, H, N, and He are the minor elements in the core. We show [7] that FPMD calculations lend strong support to the classical geochemical mass balance approach in accessing light elements in the core [3]. The impact of lower carbon content to the siderophile and chalcophile element distribution in the Earth's core and mantle (e.g. core pumping of Pb) will need to be critically evaluated. And the helium partition coefficient of ~10^{-2} makes the core a plausible source of primordial helium alternative to the undifferentiated lower mantle [8].

[1] Rudge et al. (2010) *Nature Geosci* **3**, 439. [2] Zhang & Guo (2009) *GRL* **36**, L18305. [3] McDonough (2003) *Treatise Geochem* **2**, 547. [4] Rubie et al. (2011) *EPSL* **2**, 301. [5] Birch (1952) *JGR*, **57**, 227. [6] Yin et al (2002) *Nature* **418**, 949. [7] Zhang and Yin (2012) *Nature Comm.* submitted. [8] Jephcoat et al. (2008) *Phil Trans R Soc A* **366**, 4295.