

## Prospects for an archaeal lipid paleobarometer

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Understanding the relationship between Earth's temperature and atmospheric carbon dioxide (CO<sub>2</sub>) concentration is essential to climate research. All estimates of *p*CO<sub>2</sub> from >1 Ma rely on proxy reconstructions, each with different uncertainties and underlying assumptions. Despite efforts to expand the types of geologic samples these proxies are based on, there is no consensus about the most accurate history of Cenozoic *p*CO<sub>2</sub> [1]. Recently we proposed a proxy based on archaeal lipids,  $\epsilon_{Ar}$  [2, 3]. Like the phytoplankton proxy  $\epsilon_P$ ,  $\epsilon_{Ar}$  is based on lipids recovered from marine sediments;  $\epsilon_{Ar}$  represents the carbon isotopic difference between seawater HCO<sub>3</sub><sup>-</sup> and crenarchaeol, a product of Thaumarchaeota ( $\epsilon_{Ar} = \delta^{13}C_{HCO_3} - \delta^{13}C_{cren}$ ). The proxy rationale is derived from empirical field observations [2] and from a corroborating theoretical model [3]. In the marine water column,  $\epsilon_{Ar}$  correlates significantly with all measures of respiration intensity, including increased CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> concentrations and decreased O<sub>2</sub>. In contrast to  $\epsilon_P$ , values of  $\epsilon_{Ar}$  become larger at low CO<sub>2(aq)</sub> [2]. Because Thaumarchaeota use the bicarbonate-requiring 3-hydroxypropionate/4-hydroxybutyrate (3HP/4HB) pathway of carbon fixation, we proposed that they are dependent on CO<sub>2</sub> diffusion, followed by intracellular catalysis to HCO<sub>3</sub><sup>-</sup>. Thus,  $\epsilon_{Ar}$  should be a function of both CO<sub>2(aq)</sub> and growth rate [3]. We will discuss the resulting prospects and limitations for paleobarometry, including its likely useful range (200 – 1500 ppm *p*CO<sub>2</sub>) and sources of uncertainty.

[1] Beerling DJ, Royer DL (2011) Convergent Cenozoic CO<sub>2</sub> history. *Nature Geoscience* 4, 418-420. [2] Hurley, S.J., et al. (2019) CO<sub>2</sub>-dependent carbon isotope fractionation in Archaea, Part II: Natural marine planktonic populations. *GCA*, in review. [3] Pearson A, et al. (2019) CO<sub>2</sub>-dependent carbon isotope fractionation in Archaea, Part I: Modeling the 3HP/4HB pathway. *GCA*, in review.