Novel multiproxy approaches for simultaneous environmental and seawater chemistry reconstruction

David Evans, *Earth Sciences, St Andrews University, United Kingdom*
(d.evans@yale.edu)
Hagit Affek, The Hebrew University of Jerusalem, Israel; Jonathan Erez, The Hebrew University of Jerusalem, Israel; Michael Henehan, Yale University, USA; Laura Cotton, The University of Hong Kong, Hong Kong SAR; Paul Pearson, Cardiff University, UK; Wolfgang Müller, Royal Holloway University of London, UK; Willem Renema, Naturalis Biodiversity Center, The Netherlands; Pincelli Hull, Yale University, USA; Yair Rosenthal, Rutgers University, USA

Given that a wide variety of marine geochemical data underpins a substantial portion of our knowledge of past climate, a comprehensive understanding of the applicability and limitations of such proxies is of fundamental importance. Whilst often related to a dominant environmental variable, virtually all geochemical proxy systems suffer from secondary biases. Of these, the control that seawater isotopic, elemental and carbonate chemistry exert on skeletal proxies is becoming relatively well understood (or at least, well calibrated), and yet is often overlooked because accurate reconstructions of secular variation in seawater chemistry are broadly lacking. Obtaining such reconstructions is of critical importance to both orbital and geological-scale data sets. For example, foraminifera Mg/Ca ratios are widely utilised for palaeotemperature reconstruction, and are often considered to be relatively precise on glacial-interglacial timescales when seawater elemental chemistry can be broadly considered invariant. However, a growing body of evidence [e.g. 1] suggests that Mg incorporation is dependent on seawater carbonate chemistry, with clear implications for possible glacial-interglacial bias. In deeper time, shifts in the major and trace element composition of seawater may result in large systematic biases when interpreting systems calibrated in the modern ocean.
Here, we demonstrate that a combined approach utilising careful laboratory cultures, fossil datasets and ontogenetic modelling of calcification can improve the accuracy of proxy systems. Moreover, coupling existing and emerging proxies, such as Mg/Ca and clumped isotope thermometry, can simultaneously result in temperature and seawater chemistry reconstructions for the first time. Using the Plio-Pleistocene and Eocene-Oligocene Transition as examples, these techniques provide evidence that sustained climatic change is likely to be associated with a shift in seawater chemistry [2]. However, as well as implying that existing records require revision, this change can be utilised to understand the cause of major climatic transitions. Finally, we present a novel proxy for past ocean chemistry – the foraminifera sodium/calcium (Na/Ca) ratio – which is sensitive principally to ocean calcium concentration by virtue of the extremely long residence time of sodium in seawater. Coupling Na/Ca with other trace element and clumped isotope measurements of carbonates therefore offers a method of direct reconstruction of seawater temperature and ionic composition, enabling the processes underlying such changes to be examined at unprecedented resolution.
[1] Evans, Wade, Henehan, Erez, Müller [2016]. Climate of the Past 12: 819
[2] Evans, Brierley, Raymo, Erez, Müller [2016]. EPSL 438:139