

A Multi-Proxy Approach to Tracking Ocean Chemistry over the last 1000 Ma

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First order trace element (TE) concentrations in the past oceans are controlled by several factors including; composition of eroded source rocks, oxygen and carbon dioxide contents of the atmosphere, pH, temperature, salinity, organic productivity and trace element adsorption capacity. Our recent investigating the Laser Ablation-ICPMS trace element chemistry of marine pyrite have tracked TE variations in the oceans, through the Proterozoic and Palaeozoic, and related these to cycles of bio-essential nutrient concentrations, pO₂ variations in the atmosphere and mass extinction events [1-3]. Certain TE are essential for life (eg, Ni, Cu, Co, Mn, Zn, Se) and have controlled evolutionary pathways [4], other TE are redox sensitive (eg, Se, Mo, Au), and have been used as proxies for pO₂, several TE are sensitive to variations in atmosphere/ocean pCO₂ (e.g. Cu and U), whereas still others are sensitive to ocean acidity (eg, Ag, Zn, Pb, Bi, Cd, Sb).

Here we outline a multi-proxy approach, using a variety of trace elements and their ratios, from our marine pyrite database. The data indicate broad first orders cycles of concentrations of ocean trace elements that form an internally consistent pattern over the last 1000 Ma. We interpret these cycles to indicate there have been basically two end member ocean conditions. Warm, nutrient-rich oceans, with relatively low pH (7 to 7.8) that formed under an elevated pCO₂ atmosphere, are evident in Early to Mid Cambrian, Late Silurian to Mid Devonian, Mid Carboniferous and Mid-Late Permian. The other end member is cool nutrient-poor oceans, with a more alkaline pH (7.8 to 8.4), formed during periods of low atmosphere pCO₂, which dominated the Cryogenian to Ediacaran, Ordovician, Late Devonian to Early Carboniferous, Early Permian and much of the Mesozoic. The nutrient poor, more alkaline ocean condition, broadly correlates with periods of maximum carbonate reef development, include all the global glaciation events, and three of the five mass extinction events

- [1] Large R.R. et al (2014), *EPSL* 389, 209-220.
- [2] Large R.R. et al (2015) *Gond. Res.* 28, 1282-1293.
- [3] Long J.A. et al. (2015) *Gond. Res.* 28, on-line
- [4] Williams, R.J.P. and Rickaby, R.E.M., 2012, Royal Society of Chemistry, Cambridge, UK, 319p