The Mesozoic seas incarnadine: trace metal availability and the transition from green to red algal dominance

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The reconstruction of Phanerozoic seawater chemistry based on mineral proxies is challenging. However an alternative approach using the memory harboured by the protein encoding genes of modern algae may be used. It has been hypothesised that different algal endosymbionts, originating at different geological times, impart contrasting trace metal requirements to their host. The fossil record shows that the transition from the Paleozoic to the Mesozoic is accompanied by a stark evolutionary shift in the dominant algal group from green plastid containing algae to those containing a red plastid, specifically the dinoflagellates, coccolithophores and later, the diatoms [1]. Such an algal revolution has been attributed to a better match between the trace metal availability of the more highly oxygenated Mesozoic surface waters and the contrasting trace metal quotas of the red versus the green chloroplast containing marine algae [2]. The green algal superfamily seems to contain more Cu, Zn and Fe, metals more abundant in poorly oxygenated waters, versus the red superfamily that contain a greater proportion of Cd, Co and Mn.

However, this hypothesis is open to question. Little concensus exists regarding ocean oxygen changes across the Mesozoic. Further, the inference of trace metal requirements between algal groups is based on metal quotas of whole cell digests. Yet cellular metal uptake does not equate to cellular metal use, as inadvertent assimilation is rife among the similarly sized and charged trace metals [3].

Here, we develop protocols which allow us to determine the trace metal abundance in proteins of different algal groups. We couple these new insights of trace metal requirements with novel constraints on changing ocean oxygenation based on I/Ca and algal cellular morphology to shed new light on the seawater chemical transition at the Triassic/Jurassic boundary.

[1] Falkowski P. G., *et al.,* in "Coccolithophores: from molecular processes to global impact" Springer, 429-453, (2004) [2] Quigg, A., *et al.,* Nature, 425, 291-294, (2003) [3] Horner, T. J., *et al.,* PNAS, 110, 2500-2505, (2013)