Redox-sensitive metals in red shales: Exploring a new archive for palaeoceanographic reconstruction

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The reconstruction of past environmental conditions is crucial for comprehending the mechanisms leading to extreme peturbations of the ocean–atmosphere system, which in turn will have a direct bearing on predicting the nature of future climate change. Reconstructions based on the measurement of metals and their stable isotopes in marine sediments have recently emerged, providing important new constraints on past environmental changes during the 'Great Oxidation Event' of the late Proterozoic, the 'Oceanic Anoxic Events' (OAEs) of the Mesozoic and the 'thermal maxima' of the Cenozoic. These records, however, are based almost exclusively on organic-rich black shale and carbonate archives, which have certain disadvantages. For example, black shales may be perturbed by local redox conditions or located in restricted basins that obscure global signatures, whereas lithified carbonates may be prone to diagenetic alteration, complicating the interpretation of the results.

In this study, we explore the potential of the authigenic, seawater-derived iron oxide component of oceanic 'red-beds' as a new archive of past environmetal conditions to complement the datasets derived from other lithologies. Such a methodology is especially important for mid- to high-latitude sites, where black shales and carbonates may not be preserved. Our record originates from an open-marine red-bed spanning OAE-2 (~94 Ma) in New Zealand, formerly deposited at high latitudes in the palaeo-Pacific Ocean.

A series of acid-leaching experiments using reagents of progressively increasing strength has been conducted to determine the optimal method for isolating the authigenic fraction from the red-bed lithology. Chemostratigraphic records form a suite of redox-sensitive and bioactive metals (e.g. U, Fe, Mo, Cr, V, Cu, Ni, and Zn), as well as the $^{238}U/^{235}U$ ($\delta^{238}U$) palaeo-redox tracer, have been derived in order to characterise the degree of water-column oxygenation and productivity in the palaeo-Pacific Ocean during OAE-2, for which few constraints are currently available.