

Multiproxy constraints on redox conditions of ~2.7 Ga oceans

J. YANG¹, A. L. ZERKLE¹, N. V. GRASSINEAU²,
E. G. NISBET², G. IZON¹, M. HUNTER³ AND T.
MARTIN⁴

¹Department of Earth and Environmental Sciences,
University of St Andrews, St Andrews, Fife,
KY16 9AL, Scotland, UK

²Department of Geology, Royal Holloway,
University of London, Egham TW20 OEX, UK

³Department of Earth Sciences, Cambridge
University, Downing Street, Cambridge CB2 3EQ,
UK

⁴6 Autumn Close, Greendale, Harare, Zimbabwe

It has been proposed, yet remains debated, that free oxygen might have been locally available to enable the establishment of aerobic biogeochemistry in the Neoproterozoic eon prior to the GOE. Here we present bulk-rock multiproxy geochemical analyses of well-preserved ~2.7-billion-year-old sediments of the Manjeri Formation, from the Belingwe greenstone belt in southern Zimbabwe, to reconstruct the ocean redox chemistry during this time. Iron (Fe) speciation analyses (Fe_{HR}/Fe_T and Fe_{Py}/Fe_{HR}), reflecting water-column redox conditions at the time of deposition, show large variations throughout the studied sections, with the majority of samples exhibiting elevated Fe_{HR}/Fe_T (> 0.38) and low Fe_{Py}/Fe_{HR} , indicating deposition from anoxic, ferruginous (Fe (II)-rich) water. However, a few samples show a hint of oxic conditions, with Fe_{HR}/Fe_T values below the oxic/anoxic threshold of 0.22. This is compatible with a wide range of carbon (C) and sulphur (S) isotope values that point to complex metabolic consortia in the deep waters, consistent with the involvement of both aerobic and anaerobic processes. Interestingly, some samples from shallow-water deposits display contrasting geochemical signals, with high Fe_{HR}/Fe_T values indicative of anoxic depositional conditions along with $\delta^{13}C$ and $\delta^{34}S$ values suggestive of aerobic metabolic activity. Collectively, our data suggest stratified paleo-redox conditions and complex microbial ecosystems in the Manjeri depositional environment and at least localized O_2 production in the oceans dating back to 2.7 billion years ago.