

I/Ca ratios in marine carbonate as a palaeo-redox proxy during oceanic anoxic events

ZUNLI LU¹, HUGH C. JENKYN¹
AND ROSALIND E.M. RICKABY¹

¹Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR, UK, Zunli.Lu@earth.ox.ac.uk

Periods of globally distributed extreme oxygen depletion, so-called Oceanic Anoxic Events (OAEs), have been recognized in the Mesozoic geological record and appear characteristic of episodes of extreme warmth. Here we explore the application of iodine to calcium ratios (I/Ca) in marine carbonate as a new geochemical proxy to constrain seawater redox change, and provide additional insights into the response of ocean chemistry to ancient climatic warming. Iodine has long been known as a redox-sensitive and biophilic element, mainly present as iodate and iodide in seawater, with the former converting to the latter under anoxic conditions. Laboratory experiments growing carbonate crystals from solutions spiked with iodate show that this is the ionic species incorporated into the carbonate structure, likely substituting for the CO₃²⁻ ion. A fall in the I/Ca ratio measured in carbonates formed in shallow water by marine calcifiers during the Early Toarcian and Cenomanian–Turonian OAEs is interpreted both as a response to a decrease in the iodate:iodide ratio in ocean waters and the drawdown of the global iodine inventory under conditions of accelerated organic-matter burial. The results suggest that I/Ca ratios in carbonates may be used to monitor seawater oxidation levels throughout Earth history.

Bioreduction of nitrobenzene, natural organic matter and hematite by *Shewanella putrefaciens* CN32

F. LUAN AND W. BURGOS*

Dept. Civil Environ. Eng., Penn State Univ., University Park, PA 16802, USA (ful6@psu.edu, *correspondence: wdb3@psu.edu)

We examined the reduction of nitrobenzene by *S. putrefaciens* CN32 in the presence of natural organic matter (NOM) and hematite. Bioreduction experiments were conducted with combinations and varied concentrations of nitrobenzene, soil humic acid, Georgetown NOM, hematite, and CN32. Abiotic experiments were conducted to quantify nitrobenzene reduction by biogenic Fe (II) and by bioreduced NOMs. We show that CN32 can directly reduce nitrobenzene. Both NOMs enhanced nitrobenzene reduction and the degree of enhancement depended on properties of the NOMs. Hematite enhanced nitrobenzene reduction by indirect reaction with biogenic-Fe (II), however, enhancement was dependent on the availability of excess electron donor. Under electron donor-limiting conditions, reducing equivalents diverted to hematite were not all transferred to nitrobenzene. In systems that contained both NOM and hematite we conclude that NOM-mediated reduction of nitrobenzene was more important than Fe (II)-mediated reduction. Our conclusion agrees and contrasts with related studies. Hofstetter *et al.* (1) concluded that TNT reduction by solid-associated Fe (II) was more important than by reduced quinones, while Zhang and Weber (2) concluded that CNAzB reduction occurred through a solution phase pathway via reduced NOM, and Kwon and Finneran (3) concluded that RDX reduction occurred concurrently by both solid-associated Fe (II) and reduced quinones. Differing conclusions drawn from these studies highlight the difficulty in generalizing contaminant behavior in increasingly complex systems but also highlight the need for additional research in this area.

[1] Hofstetter *et al.* (1999) *Environ. Sci. Technol.* **33**, 1479–1487. [2] Zhang & Weber (2009) *Environ. Sci. Technol.* **43**, 1042–1048. [3] Kwon & Finneran (2009) *Environ. Eng. Sci.* **26**, 961–971.