

Biogeochemical controls of iron isotope fractionation in organic-rich sediments

ALAN MATTHEWS¹, HELEN S. MORGANS-BELL²,
SIMON EMMANUEL³, HUGH C. JENKYN²,
LUDWIK HALICZ⁴ AND YIGAL EREL¹

¹Institute of Earth Sciences, Hebrew University of Jerusalem,
91904 Jerusalem, Israel (alan@vms.huji.ac.il
yerel@vms.huji.ac.il)

²Department of Earth Sciences, University of Oxford, Parks
Road, Oxford OX1 3PR, UK (helenm@earth.ox.ac.uk
hughj@earth.ox.ac.uk)

³Department of Environmental Sciences and Energy Research,
Weizmann Institute of Science, Rehovot, Israel
simon@wiseman.weizmann.ac.il

⁴Geological Survey of Israel, 30 Malchei Israel St., 95501
Jerusalem, Israel (ludwik@mail.gsi.gov.il)

This study explores the fractionation of iron isotopes (⁵⁷Fe/⁵⁴Fe) in an organic-rich mudstone succession, focusing on core and outcrop material sampled from the Upper Jurassic Kimmeridge Clay Formation type locality in south Dorset, UK. Two main types of iron-bearing assemblage are defined: mudstones with calcite ± pyrite ± siderite mineralogy, and ferroan dolomite (dolostone) bands. Mudstones and dolostones comprising the core section show a cyclic variation in isotopic composition, with lower values ($\delta^{57}\text{Fe}$ (IRMM-14) ~ -0.4 to 0.1 ‰) associated with the pyrite/ siderite-bearing mudstones, and higher values (~ -0.1 to 0.5 ‰) related to the ferroan dolostones. Pyrite nodules and pyritized ammonites from the type exposure yield $\delta^{57}\text{Fe}$ values of -0.3 to -0.45 ‰, whereas the $\delta^{57}\text{Fe}$ values of the lithogenic source Fe(III) oxides represented by samples of Mid-Late Jurassic Fe(III) oxides, range from 0.2 to 0.9 ‰. Two fractionation models are proposed to account for the $\delta^{57}\text{Fe}$ variations. These relate the lower $\delta^{57}\text{Fe}$ pyrite and siderite values to variable degrees of biogenic reduction of the isotopically heavier lithogenic Fe(III) oxides. A consequence of this reductive dissolution is that a ⁵⁷Fe-enriched iron species may be produced that may be available for the formation of the higher $\delta^{57}\text{Fe}$ dolostones. However, an isotopic profile across a dolostone band sampled in both the core and type section reveals distinct zonal variations in $\delta^{57}\text{Fe}$, characterized by two peaks, respectively located above and below the central part of the band. This form of isotopic zoning is predicted in a one-dimensional model of diffusional-chromatographic exchange. Alternative zoning models envisage the infiltration of dissolved ferrous iron from variable $\delta^{57}\text{Fe}$ sources during dolostone growth.

The study shows that lithogenous source iron is partitioned into lower and higher $\delta^{57}\text{Fe}$ minerals during deposition of the organic-rich sediments. The isotopic fractionation is driven by biogeochemical processes, but physical processes of remobilization are a marked feature of subsequent diagenetic evolution.

Nature of rare earth element abundances in shallow marine platform carbonates

A. MAZUMDAR

Geologisch-Paläontologisches Institut und Museum,
Westfälische Wilhelms-Universität Münster, Münster
anmaz2001@yahoo.com

Due to their unique 4f electron configurations, rare earth elements (La to Lu) behave as a coherent group and appear together in most geological processes. REEs in marine carbonate rocks have been studied by various workers to understand paleo-oceanic redox processes, reconstruction of paleo-oceanic REE abundance by calculating K_d and effects of diagenetic process on REE abundances.

In the present work we have determined the REE abundances in carbonate (limestone and dolomite) rocks from two late Neoproterozoic shallow marine platform carbonate sequences from India. The fundamental objectives of this paper are: (a) to portray the marked variations in REE abundance patterns in shallow marine continental platform carbonates, (b) to classify the REE abundance patterns into groups based on chondrite-normalized elemental ratios and curvatures of the abundance patterns, and (c) to discuss the possible physico-chemical factors which could have affected the nature of REE abundances.

The chondrite-normalized REE abundances in Krol and Bilara carbonates exhibit variable tetrad character. Based on chondrite-normalized Gd/Ho, La/Nd ratios, we have been able to classify the Krol and Bilara carbonates into three groups. (Y/Ho) and (Y/Dy) concentration ratios have been shown to reflect a combined effect of Y fractionation relative to neighboring trivalent REEs during carbonate precipitation from seawater and influence of continental contributions with chondritic ratios. The contrasting behavior of Y has been related to its different electronic configuration which determines its complexation behavior and partition coefficient. Ce anomaly values reported in this work are in agreement with the Ce anomalies in typical shallow marine conditions. However, absence of Ce anomaly and distinct positive anomalies in some cases reflect post-depositional Ce mobilization during early diagenesis possibly related to diagenetic mobilization of Fe and Mn.