

## Delta $^{34}\text{S}$ of discrete authigenic framboidal pyrite: A powerful palaeo-indicator for barrier estuary closure

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This study relates microscale isotopic variability of discrete authigenic framboidal pyrite to the palaeo-depositional conditions of a barrier-estuary on the east coast of Australia. Light sulfur isotope ( $^{32}\text{S}$ ) is preferentially utilised in microbially mediated pyrite formation, with the extent of fractionation dependent on how 'open', or 'closed', the depositional environment is to a replenishing supply of sulfate. An open system has an unlimited supply of the preferred, light sulfate during sedimentation. In a closed system, all of the sulfate, light and heavy (i.e.  $^{34}\text{S}$ ), is eventually utilised.

Intact sediment cores were collected from the lower Richmond River floodplain. Sampling encompassed the last 6000 years of sedimentation, extending to a depth of 5m. The isotope composition of discrete pyrite framboids was determined on select layers using secondary ion mass spectrometry[1]. The striking result was an anomalous enrichment of  $^{34}\text{S}$  in pyrite at 1.7- 2.5m depth, with  $\delta^{34}\text{S}$  peaking at +50‰. (-20 to +10‰ is the normal range for estuarine sediments). The microscale isotopic variability between pyrite framboids in this layer had a broad distribution, consistent with that theoretically predicted by Seal and Wandless<sup>[1]</sup> for a 'closed' system. This study provides the first demonstration of microscale sulfur isotope frequency distribution as a tool for identifying in the sediment record, periods of closure of barrier estuaries or other coastal embayments to marine influences.

[1]. Seal, Wandless (2006), *Reviews in Mineralogy and Geochemistry*, **61**, 633-670.

## Nitrogen cycle in the late Archean ferruginous ocean

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The Hamersley Group comprises a Late Archean sedimentary succession, which is thought to record the prelude to the atmospheric oxygenation in the early Paleoproterozoic, the so-called Great Oxidation Event (GOE) dated at around 2.4 Ga. In the present work, drill-core samples of sedimentary rocks from the upper Mount McRae Shale and Brockman Iron Formation deposited before the GOE at ~2.5 Ga were examined in order to characterize the environments and ecosystems prevailing during their deposition. We analyzed the concentration and isotopic composition of C in carbonate and organic matter, bulk N content and its isotopic composition, and major element concentrations.

The  $\delta^{13}\text{C}_{\text{carb}}$  values, ranging from -10.7 to -3.2 ‰, reflect diagenetic carbonate precipitation, with markedly negative values representing Fe-rich carbonates formed via organic matter mineralization with ferric oxyhydroxides. In contrast,  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  values record primary isotope signatures derived from ancient living organisms. The near constant  $\delta^{13}\text{C}_{\text{org}}$  values at  $-28.7 \pm 0.8$  ‰ are interpreted as reflecting photoautotrophs thriving on a large pool of dissolved inorganic carbon. Whole-rock N analyses show highly variable concentration, between 1.3 and 785 ppm, and  $\delta^{15}\text{N}$  values range between 0.4 and 13.4 ‰. Inverse relationship between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values characterize the Brockman Iron Formation. We propose that N and C biogeochemical cycles were connected via Fe redox processing in the water column and in sediments of the Late Archean ocean. Several models coupling N and Fe biogeochemical cycles are considered involving different redox states of the water column. Similar positive  $\delta^{15}\text{N}$  values might record very different N biogeochemical cycles under fully anoxic, redox-stratified, and oxic conditions of the ocean. Interpretation of N isotopes in terms of N biogeochemical cycle thus requires independent constraints on the redox structure of the ocean.