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Pyrite trace-element and sulfur isotope geochemistry of paleo-mesoproterozoic McArthur Basin: Proxy for oxidative weathering

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Abstract

Redox-sensitive trace elements and sulfur isotope compositions obtained via in situ analyses of sedimentary pyrites from marine black shales are used to track atmosphere-ocean redox conditions between ~1730 and ~1360 Ma in the McArthur Basin, northern Australia. Three black shale formations within the basin (Wollogorang Formation 1730 ± 3 Ma, Barney Creek Formation 1640 ± 3 Ma, and Upper Velkerri Formation 1361 ± 21 Ma) display systematic stratigraphic variations in pyrite trace-element compositions obtained using LA-ICP-MS. The concentrations of several trace elements and their ratios, such as Se, Zn, Se/Co, Ni/Co, Zn/Co, Mo/Co, Se/Bi, Zn/Bi, Ni/Bi, increase from the stratigraphically lower Wollogorang Formation to the Upper Velkerri Formation. Cobalt, Bi, Mo, Cu, and Tl show a consistent decrease in abundance while Ni, As, and Pb show no obvious trends.

We interpret these trace element trends as a response to the gradual increase of oxygen in the atmosphere-ocean system from ~1730 to 1360 Ma. Elements more mobile during erosion under rising atmospheric oxygen show an increase up stratigraphy (e.g., Zn, Se), whereas elements that are less mobile show a decrease (e.g., Co, Bi). We also propose the increase of elemental ratios (Se/Co, Ni/Co, Zn/Co, Mo/Co, Ni/Bi, and Zn/Bi) up stratigraphy are strong indicators of atmospheric oxygenation.

Sulfur isotopic compositions of marine pyrite ($\delta^{34}S_{pyrite}$) from these formations, obtained using SHRIMP-SI, are highly variable, with the Wollogorang Formation exhibiting less variation ($\delta^{34}S$ = –29.4 to +9.5‰; mean –5.03‰) in comparison to the Barney Creek ($\delta^{34}S$ = –13.8 to +41.8‰; mean +19.88‰) and Velkerri Formations ($\delta^{34}S$ = –14.2 to +52.8‰; mean +26.9‰). We propose that the shift in mean $\delta^{34}S$ to heavier values up-section corresponds to increasing deep water oxygenation from ~1730 to 1360 Ma. Incursion of oxygenated waters possibly caused a decrease in the areal extent of anoxic areas, at the same time, creating a possibly efficient reducing system. A stronger reducing system caused the $\delta^{34}S$ of the sedimentary pyrites to become progressively heavier. Interestingly, heavy $\delta^{34}S$ in pyrites overlaps with the increase in the concentration of certain trace elements (and their ratios) in sedimentary pyrites (Se, Zn, Se/Co, Ni/Co, Zn/Co, Mo/Co, Ni/Bi, and Zn/Bi). This study concludes that there was a gradual increase of atmospheric oxygen accompanied by ocean oxygenation through the first ~400 million years of the Boring Billion (1800–1400 Ma) in the McArthur Basin.

Keywords: McArthur Basin, Sedimentary pyrite, Boring Billion, trace elements, sulphur isotopes; Understanding Paleo-Ocean Proxies: Insights From In Situ Analyses