REE geochemistry of phosphate nodules from the lower Cambrian black shale sequence in the Mufu Mountain of Nanjing, Jiangsu province, China

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Phosphorus is a kind of life element, phosphate sediments probably relate to life events. In South China, phosphate nodules widely occur in early Cambrian black shale sequence in Yangtz platform. In this study, we sampled six phosphate nodules from the Lower Cambrian black shales in Mufu moutain, Nanjing, Jiangsu Province, and analyzed REE concentrations of these nodules from core to rim for each nodule. The general characteristics are as following: 1) Phosphate nodules are symmetrical in geochemistry with total REE concentrations increase from core to rim. The bulk nodule show HREE-enrichment compared with host shale and both are MREE-enriched. The outer layers of nodules are enriched in MREE and P. 2) The inner cores of nodules show seawater-like shale-normalized REE patterns except for Eu anomaly, and the outer layers of nodules display MREE-rich patterns. 3) Positive Eu anomalies are found in all nodules, and as a rule the Eu/Eu* values decrease form core to rim and they negatively correlate with total REE concentrations. The phosphate nodules were likely formed from pore fluids and grew layer by layer during host shales diagenesis. We suggest that both sediment pore water and submarine hydrothermal solution may contribute REE for the nodules. The Eu anomalies and their variations are results of changing proportions between Eu-rich hydrothermal fluid and REE-rich pore water. Alternatively, the changing Eu/Eu* from core to rim may reflect changing redox condition during nodule formation. Phosphorus in phosphate nodules may have solely originated from seawater, coagulated by ferric oxyhydroxides adsorption, enriched in seawater-sediments interface, and deposited in organic–rich basin of deep seawater. The REE characteristics of the nodules provide important insights to early Cambrian ocean enviromental changes and submarine hydrothermal activities at that time which produced extreme metal enrichments in the same black shale sequence in the whole South China.

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Mn enrichment factors, changes in paleo-redox or source material at Nazca Ridge (ODP Site 1237)

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Observations of sediments at a Nazca Ridge site (Ocean Drilling Program [ODP] Site 1237) revealed an abrupt sediment color change from grayish white in the upper 162 meters composite depth (mcd) to a fairly homogeneous pale brown at greater depth. Site lithology is comprised of siliceous microfossils in the upper 100 mcd dominated by calcareous microfossils in the lower 100 mcd, with no major lithologic change across the color boundary. Interstitial water chemistry indicated a limited influence of organic matter diagenesis, primarily in the uppermost sediments, with no changes in redox character coincident with the color change. This led us to investigate whether there is a change in paleo-redox conditions or a change in source material across this dramatic color change.

Redox sensitive metal enrichment factors (EF), relative to crustal averages, have the ability to describe the redox chemistry of the overlying water and marine sediments at time of burial. Manganese (Mn) EF >1 indicate oxic conditions, while uranium (U) EF > indicates suboxic or anoxic overlying water conditions. Here, we show new records of redox sensitive trace metals Mn and U generated from a Southeast Pacific Nazca Ridge site. These records extend to ~30 Ma over 360 mcd, recording depositional history as the site progressed eastward from a pelagic toward a hemi-pelagic oceangraphic setting.

U EF are >1 throughout the sedimentary record and range between 1.38 and 12.4, with a mean value of 4.74. Mn EF, range from 0.63 to 13.8 above the color contact boundary at ~162 mcd jumping to 7.04 to 106 below the boundary (Figure 1). This dramatic change in Mn EF, no change in U EF, and the coincident sharp color contact boundary lead us to conclude that a change in source material, not redox conditions caused this event.

Figure 1: Mn EF versus depth. Dashed horizontal line plotted is the Mn/Ti enrichment relative to $Mn/Ti_{crust} = 1$. Solid vertical line is depth at observed color change.