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Phosphate nodules from early Cambrian black shale sequence on Yangtze Platform, South China: A geochemical and isotopic investigation and implication for diagenetic fluid evolution

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Phosphate nodules show a widespread occurrence in the Lower Cambrian black shale sequence on Yangtze Platform, South China. The phosphogenesis of these kinds of nodules has been known to take place at or below the sediment-water interface [1,2]. It is suggested by many previous studies that the REE contents, the shale-normalized REE patterns, as well as Ce and Eu anomalies and Sr-Nd isotopes of the phosphate nodules may serve as useful indicators for the paleo-seawater or pore water conditions [3,4].

Major minerals in phosphate nodules include carbonate-fluorapatite and collophanite, with some associated dolomite, quartz, clay minerals, chalcedony, and organic materials (OM). The Lower Cambrian phosphate nodules in South China generally contain high abundance of rare earth elements up to 1362 ppm [5]. A detailed investigation through the core to rime of the nodules indicates a systematic variation of REE concentrations with an increase of ΣREE and $(Dy/Yb)_N$ ratios and decrease of Ce/Ce* ratios towards the rims, which may reflect an increasing water-rock interaction in the pore fluid system during the phosphate formation. Different shale-normalized REE patterns are observed for the nodules. Although many of the nodules show a hat-shape pattern that records the diagenetic remobilization and enrichment of REE, some of them still remain sea water like REE pattern together with seawater-like element ratios such as $(Dy/Yb)_N$ and Y/Ho ratios, indicating these nodules may still have preserved the primary seawater chemistry [4,6]. Negative Ce anomalies are observed with Ce/Ce* values between 0.2-0.5; those nodules with seawater-like REE patterns mostly have lower Ce/Ce* (<0.35) than those with hat-shaped patterns (>0.4). No significant Eu anomalies are observed although some of them display a slightly positive Eu, which may either reflect a strong anoxic environment or a contribution from local dispersed hydrothermal fluids in the sediments [4]. The highly varied $^{87}Sr/^{86}Sr$ ratios of the phosphate nodules may record different water-rock interaction and varying radiogenic Sr contribution from the host silicates in the marine sediments, which are unrepresentative of the primary seawater Sr isotope variation. Due to the immobile characteristic of the rare earth elements, the $^{143}Nd/^{144}Nd$ ratios generally show a limited variation with calculated εNd(t=532Ma) values mostly between -10 and -6. However, higher εNd(t) values are observed in phosphate nodules with seawater-like REE patterns, whereas those with hat-shaped REE patterns tend to display more negative εNd(t) values.

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