Rare earth elements as a proxy for redox conditions in black shales?

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Rare earth elements (REEs), most notably the Ce anomaly, are commonly used as proxy for redox conditions in modern and ancient sedimentary basins. Conversely, the REE pattern is used in understanding provenance and the conditions of post-depositional diagenesis. In black shales, the REE pattern is characterized as light rare earth element (LREE) enriched and heavy rare earth element (HREE) depleted; this distribution primarily reflects the distribution of clay minerals and source material. Often times, discrete units of black shale bed sequences, which are representative of the same depositional environment, have different REE patterns. Is it possible that the changing REE pattern reflects changes in redox conditions during sediment accumulation? Here, we present evidence of varying black shale REE pattern from the Ordovician-Silurian, Permian-Triassic, and Cenomanian-Turonian extinctions, where "event black shale" samples deviate from the bulk REE pattern. This REE pattern may reflect changes in detrital conditions (e.g., sedimentation) leading to changes in redox conditions. These "event black shale" samples differ from the average black shale chemostratigraphy by displaying a depleted REE pattern. The depleted REE patterns are aligned with other redox proxies, such as, high V/V+Ni and degree of pyritization values, as well as extremely light and enriched $\delta^{34}S$ values, which suggest "event black shales" formed under intense redox conditions. One possibility is that the depleted REE pattern may reflect water stagnation, causing the chemocline to stratify, and the pycnocline to stabilize. These two factors will lead to a distinct anoxic-oxic boundary (AOB). Near the AOB, REEs are scavenged by Fe-Mn oxyhydroxides, leading to low REE concentrations in detrital clay minerals.