A New Hypothesis for Interpreting the Sedimentary Cerium Anomaly Paleo-Redox Proxy in Oil Shale Depositional Environments: The Influence of Particulate Carrier Fluxes (Mn, Fe, Algal Tissue)

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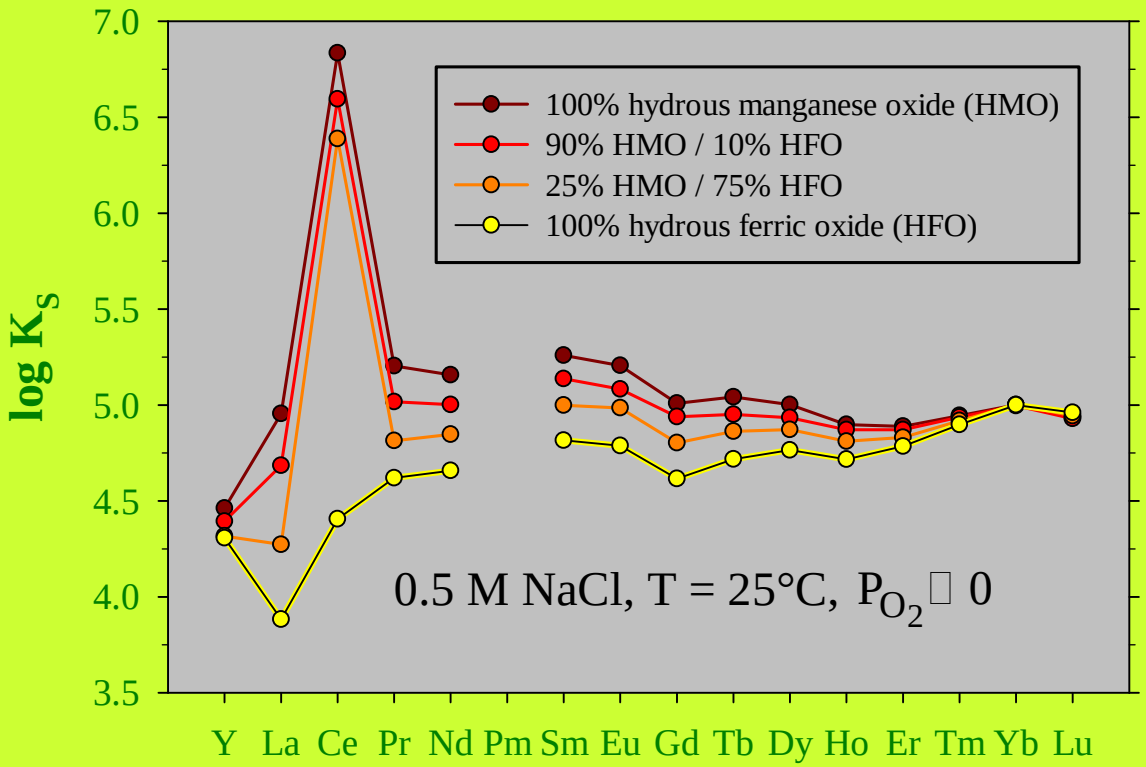
Marine geochemists have long interpreted sedimentary records of the 'Ce anomaly' as a paleo-redox proxy, believed to signify shifts in the oxygenation of ancient bottom waters that accompany geologic events like the opening of ocean basins. According to general reasoning, Ce(III) oxidation in oxygen-rich seawater gives rise to enhanced sorption of Ce(IV) on particulate carriers, ultimately resulting in positive sedimentary Ce anomalies (and *vice versa*). However, while Fe oxides and organic matter appear to record this signal faithfully, Mn oxides catalyze Ce(III) oxidation under anaerobic conditions, thus creating spurious positive Ce anomalies unrelated to ambient dissolved O_2 levels. In a study of rare earth element sorption on synthetic mixtures of hydrous Mn and Fe oxides, performed in our laboratory, the presence of just 25% HMO produced a pronounced positive Ce anomaly under a pure N_2 atmosphere. Ce anomalies may therefore primarily reflect the presence of Mn oxides in marine sediments, rendering them unsuitable as even a qualitative proxy for redox conditions in the deep paleo-ocean.



Solid-solution distribution coefficients (log K_S) for sorption of yttrium and the rare earth elements (YREEs) on synthetic mixtures of hydrous manganese oxide (HMO: $MnO_{2.01\pm0.05}$) and hydrous ferric oxide (HFO: FeOOH) at pH = 6.35±0.08. Values for Yb were matched by shifting each pattern vertically, in order to emphasize the progression of shapes from pure HFO to pure HMO. Note the incongruous behavior of Ce.