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Rare-Earth Elements and Trace Metals as Proxies of Paleo Redox and Paleo Prmary Productivity for the Phosphoria Formation—A Marine Phosphate Deposit of Permian Age

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The depositional history of the Phosphoria Formation, a world-class sedimentary phosphate deposit that extends over approximately 300,000 km^2, has been ascertained from its trace-element and major-element-oxide composition. The deposit, centered in southeast Idaho, includes two major ore zones and an intervening waste zone. The oceanographic conditions under which they accumulated were likely similar to conditions under which many sedimentary phosphate deposits were deposited, but also to conditions under which black shales accumulated that commonly contain little phosphate. A shortcoming shared by many earlier studies of these deposits, to interpret fully the trace-element record, has resulted from a failure to examine the marine fraction of elements totally separate from the terrigenous fraction.

The rare-earth element (REE) patterns of the bulk sediment from the deposit, obtained by normalizing elemental concentrations to a shale standard, reflect two REE sources—seawater and terrigenous debris. When compared to REE distributions in the Black Sea, Cariaco Basin, and the eastern Pacific Ocean, the elevated REE concentrations in the Phosphoria Formation suggest that bottom water in the Phosphoria Sea was oxygen depleted, to the point of being denitrifying. This water-column chemistry was established by a balance between the bacterial oxidation of organic matter settling into the bottom water from the photic zone and advection of bottom water between the basin and open ocean.

Within the marine fraction alone, the two ore zones have greater Yb/Sm, Tm/Sm, and Er/Sm (heavy REE) means than the center waste zone at the 90% confidence interval, and different variances. No differences are seen between the ore and waste zones in their Nd/Sm, Gd/Sm, and Ho/Sm ratios. The enrichment of the heavy REE in the ore zones, relative to the lighter REE, represents a stronger deep-ocean REE pattern for the ore zones than for the center waste, suggesting a more robust exchange of water with the open ocean during deposition of the ore zones and likely greater upwelling of nutrient-enriched water into the photic zone. However, estimated rates of accumulation of marine Ni and P_2O_5, both of which have a biogenic source, show that primary productivity was high throughout deposition of the deposit.

These interpretations of the biology, geochemistry, and hydrology of the Phosphoria Basin are supported by progressively greater ratios in the marine fraction of Cr$>$V$>>$Mo to Ni; for which marine Cr, V, and Mo commonly have a dominantly O_2—depleted, bottom-water source and Ni a photic-zone, largely algal source. The approach of the marine Cr:Mo and V:Mo ratios to present-day seawater values at high Mo concentrations, more so in the center waste than in the ore zones, further indicates variable bottom-water redox conditions that were, nonetheless, denitrifying during deposition of the ore zones and denitrifying to SO_4^{2-}reducing during deposition of the center waste zone, a reflection of the advection of bottom water.