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Rare-Earth Element Enrichment as a Function of Water Depth in Recent Growth of Pacific Ferromanganese Crusts

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Ferromanganese (Fe-Mn) crusts are submarine hydrogenetic oxide deposits that are precipitated out of the ambient seawater. These rock deposits are prevalent throughout Earth's ocean basins, form over millions of years, and sequester many trace elements, including some metals at grades of economic interest; in particular, rare-earth elements (REEs) are enriched in Fe-Mn crusts relative to average upper continental crust [1]. Here we evaluate the concentrations of REEs in the most recent growth layer of Pacific Ocean ferromanganese crust samples as a function of water depth. Samples for this study were collected with remotely operated vehicle (ROV) Hercules aboard four E/V Nautilus cruises (NA110, NA114, NA135, NA137) spanning latitudes from 1°S to 22°N. Top scrapes (the top <1mm of outer crust) of each rock sample were analyzed for REE contents after acid digestion using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). We compared REE contents of each rock sample with water column property data (salinity, temperature, oxygen, and depth) collected with CTD on ROV Hercules at each point of sample collection, providing high spatial accuracy for crusts and their immediate chemical environment in the water column. Our data confirmed generally large, positive Ce anomalies that are a signature of Fe-Mn crusts [2], and that the largest Ce anomalies are associated with shallow water depths. Contrastingly, high REE concentrations other than Ce are associated with samples collected at deeper water depths. These REE trends observed in recent growth in Pacific Fe-Mn crusts mirror those of REE depth profiles in seawater [3], suggesting that REE behavior in modern seawater has remained stable on average over the time scale of uppermost crust layer accumulation, which may span up to 1Myr.

[1] Goldschmidt, Hein & Koschinsky (2014), *The Treatise on Geochemistry*, v. 12, 273-291

[2] Goldschmidt, Bau et al., (2014), *Chemical Geology* 381, 1-9

[3] Goldschmidt, Alibo & Nozaki, (1999), *Geochimica et cosmochimica acta* 63.3-4, 363-372