Controls on La and Ce enrichment in marine ferromanganese crusts

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In order to decipher the controls on rare earth elements in ferromanganese crusts, we construct a conceptual model composed of five stages to describe the enrichment process of La and Ce: (1) Diffusion in seawater and sorption; (2) Equilibrium between sorption and desorption; (3) Diffusion in pore water of crusts; (4) Phosphatization, the incorporation of phosphate; and (5) Diffusion in the phosphatized crust layers. Based on a systematic analysis, we suggest that seven factors control the La concentration in Fe-Mn crusts including mineral concentration $(MnO_2+FeOOH)$, element ratios (Mn/Fe), distribution coefficient of REY between and ferromanganese oxides (K_s) , seawater concentration of free hydrated REY ions in seawater $[M^{3+}]$, temperature (T) and pH (pH) both of which are capable of changing the $_{i}K_{s}$, and the incorporation of phosphate during phosphatization. The seven controls on Ce concentration in Fe-Mn crusts include mineral concentration ($MnO_2+FeOOH$), diffusivity of REY in seawater (D_{sw}), temperature (T) which is capable of changing the D_{sw} , concentration gradient of free hydrated Ce ions in seawater $(d\varrho/dx)$ -), growth rate of ferromanganese crusts (GR), specific surface area (S_{sp}) , and the incorporation of phosphate. Our analyses on the ferromanganese crusts from the Magellan seamounts suggest that the La³⁺ concentration in seawater is a major control of the concentration of La in Fe-Mn crusts in this area. Our analyses further indicate that variations of paleoseawater T, GR, S_{sp} , and subsidence and migration of the host seamounts cannot fully explain the temporal variation of Ce concentrations in Fe-Mn crusts from the Magellan seamounts, and that seawater Ce^{3+} concentration is the key controlling factor.