



Distribution of REY among major geochemical phases of Fe–Mn crusts from the South China Sea

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Marine ferromanganese (Fe–Mn) crusts are Fe–Mn (oxyhydr)oxides precipitating from seawater and they enrich transition metals and rare earth elements plus yttrium (REY). Fe–Mn crusts discovered in the South China Sea (SCS) were defined as marginal type in comparison to the open-ocean crusts. The mainly Mn-mineral of the Crust-ZSQD42A is δ -MnO₂ which is the typical mineral composition of the hydrogenetic crust growing in the oxic environment. The Crust-HYD66 contains δ -MnO₂, birnessite and todorokite, which reveals a relatively suboxic growth environment. We developed a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) line scanning method to investigate the partitioning behavior of the REY in the growing processes of the crusts. The results show that the distribution of concentrations of the main elements is consistent with the change trend of the crust layer structure and the high concentration of the main elements can represent the corresponding minerals. In Crust-ZSQD42A, there is a strong positive correlation between Fe, Mn and P, which shows the closely symbiosis of the Fe-, Mn- and P-minerals on the micron/submicron scale. REY is mainly associated with the Fe, which indicated that the REY occurred mainly in the Fe (oxyhydr)oxides. The enrichment of the REY in the typical hydrogenetic crusts is suggested to the scavenging mechanism. In contrast, Fe and Mn is negatively correlated in the Crust-HYD66-2 showing the alternate growth or crystal differentiation of the Fe-minerals and Mn-minerals. There is fractionation of the light REY and heavy REY (LREY/HREY) between the Fe–Mn oxides in Crust-HYD66-2, with the LREE and HREE preferentially bounding to Mn-oxide and Fe-oxyhydroxide, respectively. The fractionation implies the REY enrichment should attribute to their mineral composition, growth environment and the growth rate. Furthermore, the strong correlation between the P and REY in the both SCS crusts can be revealed the possible formation of the REY-phosphate in the Fe–Mn crusts.