Transfer of REE from Mn oxides to phosphates during early diagenesis in pelagic sediments

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The migration of REEs in pelagic siliceous sediments were studied, especially (i) accumulation of REEs at sea floor to Mn^{4+} oxides, (ii) release of REEs from Mn^{4+} oxides accompanied with the reductive dissolution of Mn^{4+} oxides during early diagenesis, and (iii) incorporation and fixation of REEs released from Mn^{4+} oxides to phosphates such as apatite below 0.6 meters below sea floor (mbsf). These processes have been indicated by various geochemical findings: (a) chemical compositions of bulk sediment and pore water, (b) REE patterns of bulk sediment, (c) oxidation states of Ce, Mn, and Fe and host phase of Y by XANES, and (d) chemistry of specific phases such as Mn^{4+} oxides and apatite by means of chemical leaching, LA-ICP-MS, and XANES. Reductive dissolution of Mn^{4+} oxides and reduction of Ce^{4+} to Ce^{3+} with depth were revealed by direct determination of oxidation states of Mn and Ce by XANES. The transfer of REEs released by the reductive dissolution of Mn^{4+} oxides is strongly suggested by the presence of positive Ce anomalies in apatite at 0.80 mbsf (LA-ICP-MS) and at 1.80 mbsf (chemical leaching), which must be inherited from Mn^{4+} oxides which can accumulate Ce by oxidizing Ce^{3+} to Ce^{4+}. This observation shows that apatite fixes the REEs with positive Ce anomaly once dissolved from Mn^{4+} oxides during early diagenesis. Consequently, we found that total REEs in the two phases (Mn^{4+} oxides and apatite) are preserved even after diagenetic alteration, because apatite fixes the most of the REEs released from Mn^{4+} oxides. The results indicate two geochemical implications: (i) REE abundances in apatite in sediment, which has attracted great interests in terms of REE resources, depend on the amount of REEs fixed in Mn (and Fe) oxides initially formed at the sediment surface, and then apatite finally fixes the REEs during early diagenesis; (ii) the reliability of apatite as a proxy of seawater chemistry is affected seriously by the overprint of REE signature by the diagenetic effect. However, if the contribution of REEs in Mn (and Fe) oxide is small, then the REE pattern of apatite can preserve information of the REE pattern of seawater, including the degree of Ce anomaly.

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