Nano-mineralogy and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS and TEM studies

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Rare earth elements (REE) and yttrium (Y), known as REY, have recently been found to be extremely abundant in deep-sea sediments, which may be an essential REY resource for future. However, their formation processes remain controversial. Since bioapatite is one of the most important REY hosts in REY-rich deep-sea mud, its mineralogical and geochemical characteristics are critical to be identified. By using multiple analyzing approaches of in situ chemical analysis and atomic resolution chemical imaging, this study has gained some new insights: (1) Scanning electron microscope and transmission electron microscopy observations reveal that bioapatite mainly consists of aligned hydroxyapatite nanocrystals; (2) Laser ablation-inductively coupled plasma-mass spectrometry studies show that the REY contents are not uniformly distributed within bioapatite fossils; (3) The measured data and modeling results imply that the REY contents should be incorporated into the bioapatite from seawater as well as the pore water during the early diagenesis; (4) Z-contrast imaging reveals the following two possible coupled substitutions schemes in bioapatite: $REE^{3+}+Na^{+}\leftrightarrow 2Ca^{2+}$ and/or $REE^{3+}+Si^{4+}\leftrightarrow Ca^{2+}+P^{5+}$, which is distinguished from those land-based ion-absorption-type REE mines; (5) Additionally, this study suggests that bioapatite fossils are prone to undergo alterations during early diagenesis, and thus cautious examination is required for using REE signals in bioapatite for paleoceanographic study.

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