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Enrichment of rare earth elements in siliceous sediments under slow deposition: A case study of the central North Pacific



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ARTICLE INFO

Keywords: Rare earth elements Clarion-Clipperton Fracture Zone Deep-sea sediment Biological apatite Phillipsite

ABSTRACT

As an important submarine rare earth elements (REE) exploration target, the REE-rich deep-sea mud in the Pacific Ocean has recently attracted much research attention, yet its metallogenic mechanism has not been sufficiently addressed. In this study, we conducted detailed grain size analysis, mineral identification and geochemical measurement for the MG026 sediment core in the central North Pacific. The $> 63 \, \mu m$ fraction of the samples mainly contains siliceous bioclastics, phillipsite accretions, fish teeth and bones and ferromanganese micro-nodules; the 4-63 µm fraction mainly contains the abovementioned biological detritus, together with ilmenite, quartz and zeolite; the < 4 µm fraction mainly contains barite, clay minerals, carbonate-fluorapatite and amorphous ferric hydroxide. The rare earth elements and yttrium (SREY) contents in the samples can reach 810.4 ppm, and are mainly concentrated in the biological apatite (fish teeth and bones) and the Fe-Mn oxidehydroxide on the micro-nodule surface. The grain size analysis suggests that the smaller the Mz (mean grain size), the higher the REY enrichment. The post-Archean Australian shale-normalized REE patterns are slightly HREE-enriched with significant negative Ce anomalies, indicating that the rare earth elements of the samples are mainly seawater-derived with minor terrigenous input. We conclude that the REY content is controlled by the grain size, the amount of fish teeth and sedimentation rate: With low sedimentation rate, REYs from the seawater may have mainly replaced the Ca²⁺ ions of biological apatite lattice in form of isomorphism, and minor REYs may have also adsorbed on Fe-Mn micro-nodules due to the scavenging effect. As a concurrent result of the low sedimentation rate, the mean grain size of sediment may have decreased, and abundant phillipsite may have been formed.

1. Introduction

Rare earth elements (esp. heavy rare earth elements such as Gd to Lu) and yttrium (REY) are very important for the development of information technology, biotechnology and energy technology (Service, 2010). China contains the world's highest REY reserves on land (Gambogi, 2016), and many countries (e.g., Japan) have invested immensely in exploring REE resources on the seafloor.

Previously, REEs on the seafloor were considered to be largely hosted by ferromanganese nodules and crusts (Pattan et al., 2001; Baturin and Yushina, 2007; Xue et al., 2008; Jiang et al., 2011; Kolesnik and Kolesnik, 2015). Nonetheless, Kato et al. (2011) reported that the

REY-rich deep-sea mud in the Pacific Ocean also hosts significant REY resources, with its REY content comparable or even exceed that of the ion-absorbed-type REY deposits in South China.

Compared to the comprehensive researches on REY deposits on land (Gao et al., 1999; Xu et al., 2002, 2004; Ni et al., 2003; Tian et al., 2003, 2006), studies of marine REE mineral resources are very insufficient due to the sampling difficulties. To ensure stable REE supply for the future generations, investigation of the metal source and oreforming mechanism of these seafloor REE resources are necessary.

It was long considered that phillipsite is the main controlling factor for the REE composition of deep sea sediments (Piper, 1974; Shen, 1990). However, geochemical data compilation of 2000 seafloor

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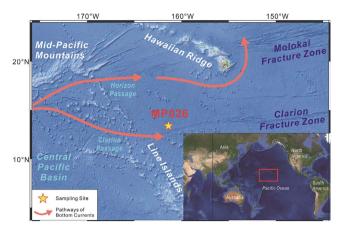


Fig. 1. Satellite image showing the geographic location of the sampling site. Satellite image from Google Earth. The pathways of bottom current are branches of Antarctic Bottom Water (AABW) modified after Glasby (2006).

sediment samples from 78 sites across the Pacific Ocean indicated that REY-rich mud (including metalliferous sediments, zeolitic clay and pelagic red clay) is mainly distributed in the eastern South Pacific and central North Pacific (Kato et al., 2011), and that hydrothermal iron-

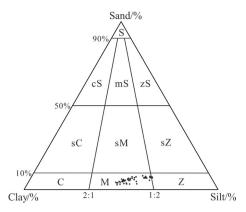


Fig. 3. Classification of sediment samples based on ternary "Folk" diagram (S- Sand; cS- clayey Sand; mS- muddy Sand; zS- silty Sand; sC- silty Clay; sM- sandy Mud; sZ- Sandy silt; C- Clay; M- Mud; Z- Silt). Base diagram is from Zhang et al. (2013a) and modified after Folk et al. (1970) and Folk (1980).

oxyhydroxides precipitated from hydrothermal plumes and phillipsite are the two main carriers of REYs. Dubinin (2000) examined the REE concentrations of the phillipsite samples (> 50-µm-fraction) from the Southern Basin of the Pacific, and found that massive rounded



Fig. 2. Photographs of bulk sediment samples.

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