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Geochemistry and mineralogy of REY-rich mud in the eastern Indian Ocean

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ABSTRACT

Deep-sea sediments in parts of the Pacific Ocean were recently found to contain remarkably high concentrations of rare-earth elements and yttrium (REY) of possible economic significance. Here we report similar REY-rich mud in a core section from Deep Sea Drilling Project Site 213 in the eastern Indian Ocean. The sediments consist mainly of siliceous ooze, with subordinate zeolitic clay that contains relatively high REY concentrations. The maximum and average total REY (ΣREY) contents of this material are 1113 and 629 ppm, respectively, which are comparable to those reported from the Pacific Ocean. The REY-rich mud at Site 213 shows enrichment in heavy rare-earth elements, negative Ce anomalies, and relatively low $Fe_2O_3/\Sigma REY$ ratios, similar to those in the Pacific Ocean. In addition, the major-element composition of the Indian Ocean REY-rich mud indicates slight enrichment in lithogenic components, which probably reflects a contribution from southern African eolian dust. A volcaniclastic component from neighboring mid-ocean ridges or intraplate volcanoes is also apparent. Elemental compositions and X-ray diffraction patterns for bulk sediment, and microscopic observation and elemental mapping of a polished thin section, demonstrate the presence of phillipsite and biogenic apatite, such as fish debris, in the REY-rich mud. The strong correlation between total REY content and apatite abundance implies that apatite plays an important role as a host phase of REY in the present deep-sea sediment column. However, positive correlations between ΣREY and elements not present in apatite (e.g., Fe_2O_3, MnO, and TiO_2) imply that the REY-rich mud is not formed by a simple mixture of REY-enriched apatite and other components.

1. Introduction

Rare-earth elements (REEs) and yttrium (together called REY) in sediments and sedimentary rocks have been used as a powerful tool for defining modern and past geological environments and processes, because of their unique behavior during various geochemical processes. In recent decades, the geochemical behavior and distribution of REY have been well documented from pelagic sediments (e.g., Toyoda et al., 1990; Murray et al., 1992; Nath et al., 1992; Fagel et al., 1997; Banakar et al., 1998; Dubinin et al., 2013), coastal sediments (e.g., Elderfield and Sholkovitz, 1987; Murray et al., 1992; Sholkovitz and Szymczak, 2000), metalliferous (Fe–Mn) sediments (e.g., Bender et al., 1971; Ruhlin and Owen, 1986; Barrett and Jarvis, 1988; Steinmann et al., 2012), hydrogenetic ferromanganese crusts and nodules (e.g., Bau et al., 1996; Pattan et al., 2001; Dubinin, 2004), marine phosphorites or phosphatized ferromanganese crusts (e.g., Bau et al., 1996; Koschinsky et al., 1997), and terrestrially exposed chert (e.g., Rangin et al., 1981; Murray et al., 1990, 1991; Kato et al., 2002; Bau and Alexander, 2009).

A recent report of “REY-rich mud” (deep-sea sediments containing high concentrations of REY) in the Pacific Ocean has led to a new appreciation of the resource potential of deep-sea sediments. Kato et al. (2011) noted five advantageous features of REY-rich mud: (1) The mud has very high total REY (ΣREY) contents, and its content of heavy REEs (HREEs) exceeds those of the southern

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Chinese ion-adsorption ore deposits that currently dominate the world's HREE reserves. (2) The REY-rich mud is widely distributed in the Pacific Ocean in volumes that could easily supply current world demands. (3) The distribution of REY-rich mud in widespread, homogeneous pelagic clay makes it easy to perform resource mapping and exploitation. (4) REY-rich mud contains very low concentrations of the radioactive elements Th and U, thus posing minimal environmental problems during mining and processing. (5) All REY elements can be readily leached from the mud by dilute acids.

The Pacific Ocean deposits of REY-rich mud occur in pelagic deep-sea regions where neither terrigenous components nor abundant biogenic carbonate or silica cause significant dilution of the REY contents (Kato et al., 2011). Kato et al. (2011) suggested that the genesis of the REY-rich mud is related to seafloor hydrothermal and volcanic activity at mid-ocean ridges. Suspended particulate Fe-oxyhydroxides from hydrothermal plumes are thought to take up REEs from ambient seawater during advection through the water column and after settlement on the seafloor (e.g., German et al., 1990), making this material an important host phase for REY in seafloor sediment. In addition, phillipsite, a common zeolite in pelagic clay with a low sedimentation rate (Stonecipher, 1976), has been suggested as a carrier of REY in Pacific sediments, based on a multivariate statistical analysis (Kato et al., 2011). However, the fundamental mechanism that concentrates REY in phillipsite is still uncertain (Kato et al., 2011). Although Piper (1974) showed enrichment of REEs in phillipsite from Pacific deep-sea sediment, Dubinin (2000) reported that REE concentrations in separate phillipsite accretions are not especially high and that phillipsite itself does not absorb REEs from seawater. Dubinin (2000) also noted that growth of phillipsite is accompanied by incorporation of Fe-oxyhydroxides, Fe–Ca-hydroxyphosphates, and microscopic bone detritus, and concluded that REE concentration in phillipsite depends on the abundance of these materials in phillipsite aggregates. Moreover, apatite composing fish bones and teeth has long been proposed as an essential host for REY in deep-sea sediment (e.g., Arrhenius et al., 1957; Bernat, 1975; Toyoda et al., 1990). And recent studies using X-ray absorption fine structure (XAFS) analysis or laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) have demonstrated that apatite is a significant contributor to REY concentrations in Pacific deep-sea sediment (Kashiwabara et al., 2014; Kon et al., 2014).

This study sought evidence of REY-rich mud in oceans other than the Pacific. We analyzed sediment samples collected by the ocean-drilling program at seven sites that cover a wide range of the Indian Ocean. This paper documents the presence of REY-rich mud in the Indian Ocean, characterizes its geochemistry, and discusses its geological implications.

2. Material

We analyzed sediment samples obtained from Deep Sea Drilling Project (DSDP) Sites 213, 223, 236, 238, and 259 and Ocean Drilling Program (ODP) Site 758A, all in the Indian Ocean, and DSDP Site 267 and 267A in the Indian sector of the Southern Ocean (Fig. 1). We analyzed samples from the seafloor to ~50 m below the seafloor (mbsf) to assess the distribution of REY near surface sediment. In addition, we analyzed samples from the core top to ~123 mbsf of DSDP Site 213 in more detail because this site has a large thickness of phillipsite-containing dark brown zeolitic clay between 75 and 123 mbsf (von der Borch et al., 1974), which is the typical lithology of the Pacific Ocean REY-rich mud.

DSDP Site 213 is at 10°12.71′S, 93°53.77′E and 5609 m water depth, in the northwestern part of the Wharton Basin east of Ninetyeast Ridge (Fig. 1). Drilling penetrated to 172.5 mbsf, and ~150 m of continuous sediment section and ~8 m of altered basalt were recovered (von der Borch et al., 1974). The sediment section was divided by von der Borch et al. (1974) into four lithological units: Unit 1 (0–70.5 mbsf) is radiolarian-diatom ooze, Unit 2 (70.5–135 mbsf) is zeolitic clay grading into nannofossil-bearing manganese iron-oxide-rich clay, Unit 3 (135–147 mbsf) is nannofossil ooze, and Unit 4 (147–152 mbsf) is iron-oxide-manganese facies. We analyzed 195 sediment samples collected with 5 cm^3 scoops every ~50 cm between the top of the core and 123 mbsf, corresponding to all of Unit 1 and the portion of Unit 2 containing the zeolite-rich clay layer (Fig. 2). Unit 1 consists of reddish-yellow radiolarian-diatom ooze with a minor fraction of clay. Unit 2 consists of zeolitic brown clay, in which well-crystallized phillipsite is the main zeolite found. The zeolite content reaches 20% around 95–114 mbsf. Iron oxide minerals and manganese micronodules are concentrated in the lower part of the unit. The base of Unit 2 grades into the underlying unit and consists of interbedded nannofossil ooze and clay, with decreasing iron oxide-manganese constituents and no zeolite (von der Borch et al., 1974). Radiolarian biostratigraphy (von der Borch et al., 1974) indicates that Unit 1 represents an apparently uninterrupted sequence from late Miocene to Quaternary time. The upper part of Unit 2 is late to middle Miocene, and the lower part of the unit is almost unfossiliferous zeolitic clay. Only core-catcher samples contain some foraminifers of middle Eocene age (von der Borch et al., 1974).

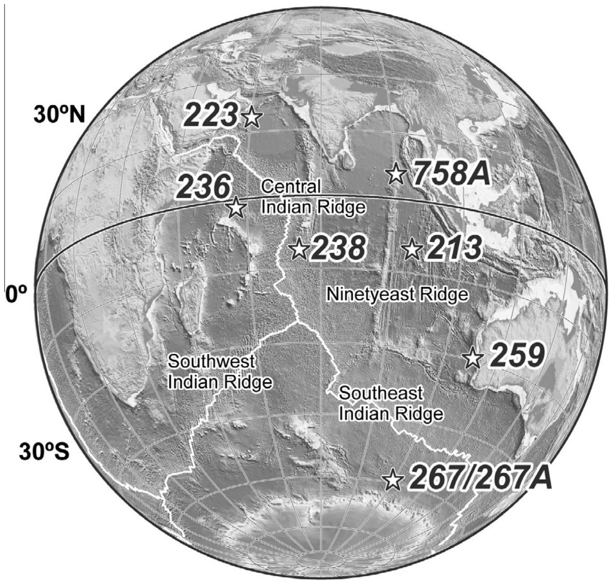

Fig. 1. Locations of drilling project sites (DSDP and ODP) analyzed in this study. Topography and bathymetry are based on 2-min gridded global relief data (ETOPO2v2; National Geophysical Data Center, 2006, http://www.ngdc.noaa.gov/mgg/fliers/06mgg01.html).

DSDP Site 223 is at 18°44.98′N, 60°07.78′E and 3633 m water depth, on the continental rise off Oman (Fig. 1). Total penetration was 740 mbsf, and total core recovery was 203.7 m. From the seafloor to 455 mbsf, the sediment consists of olive and yellow–green silty nannofossil ooze and chalk, siltstone, and diatomite (Fig. 2; Whitmarsh et al., 1974). Only two core segments were recovered from shallower than 50 mbsf, and we analyzed eight samples from this interval.

DSDP Site 236 is at 1°40.62′S, 57°38.85′E and 4487 m water depth, ~300 km northeast of the Seychelles Islands (Fig. 1). It was continuously cored from the sediment surface to 327.5 mbsf, with 218.5 m of core recovery. From the core top to 17.5 mbsf, the sediment is yellowish to gray nannofossil ooze with a layer of brown radiolarian ooze, and between 17.5 and 139.5 mbsf, it consists mainly of nannofossil ooze, foraminiferal ooze, and foram