REE and Y geochemistry in deep-sea sediments from eastern Clarion–Clipperton Zone (NE Pacific)

Геохимия на редкоземните елементи и итрия в дълбокоморски седименти от източната част на полето Кларион–Клипертон (СИ Тихи океан)

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Introduction

An expanded recent interest to the deep-sea sediments towards growing rare-earth elements (REE) use and application, and new REE resources discovering is now fast developed. Sources for REE, e.g. deep-sea sediments, nodules, crusts etc, have been explored in many different ways. It was shown that deep-sea muds contain high concentration of REE and yttrium (REY) at numerous sites throughout the eastern, south and central area of North Pacific (Kato et al., 2011). Hence, the resource value of the mud may be increased if their main metals are recovered together with REY. We present a study of deep-sea sediments from eastern Clarion-Clipperton Zone (CCZ) analysed as potential REY source.

Geological setting

The eastern CCZ (to the east of 125°W) comprises mainly the western slope of Mathematicians’ Ridge which is a part of Paleo East Pacific Rise. Volcanic structures (single volcanoes and chains of seamounts) are distributed throughout CCZ. A more subtle but very persistent bathymetric pattern of CCZ is a system of adjacent linear groups of ridges and valleys that are aligned approximately perpendicular to the bounding Clarion and Clipperton Fracture Zones. Bottom sediments comprise end members (carbonates, red-brown clays, siliceous sediments) and mixtures of them (Kotlinski et al., 2009).

Sampling and analytical techniques

Sixteen samples studied were collected from three stations during IOM-2009 cruise with 0.25 m^2 box corer equipped with SONY DSC-V1 digital camera. The stations have different geomorphological locations: station 2267 – within a wide terrace featuring complex undulating relief, at depth of 4369 m; station 3001 – on the bottom of a depression at depth of 4457 m, station 3017 – on a terrace, at depth of 4419 m. Core samples selected comprise the following layers/depth intervals: liquid-plastic to soft-plastic (geochemically active) layer/0–5 cm, soft-plastic to plastic layer/5–10 cm, and plastic layer/10–20 cm. In the laboratory samples were imaged, dried at 30 °C and split. Dried polymineral aggregates were stuck on double-side scotch tape, impregnated with epoxy resin and polished to around 30 μm for petrographic studies. Phase identification was performed by XRD. Major and trace elements content was determined by ICP-OES and LA-ICP-MS.

Results

Main components of the sediments identifiable under the microscope are clayey aggregates (ca. 60–90 vol.%), fragments of radiolarian tests (5–40 vol.%), and micronodules (1–2 up to 7 vol.%). Characteristic for stations 3001 and 2267 are sand-size chlorite flakes presented as separate flakes or up to 5 vol.%. Volcanic glass as pumice shards floating in the radiolarian-clayey groundmass was occasionally observed. According to the microscopic data the sediments are fossiliferous silty-clayey muds. In most of the samples mineral phases identified by XRD are: halite, quartz, mica (chlorite/montmorillonite/kaolinite), clay (chlorite/montmorillonite), plagioclase and K-feldspar. There was a halo (6–21° 2θ) observed that coincides with the area of picks of organic matter phases and/or of clays

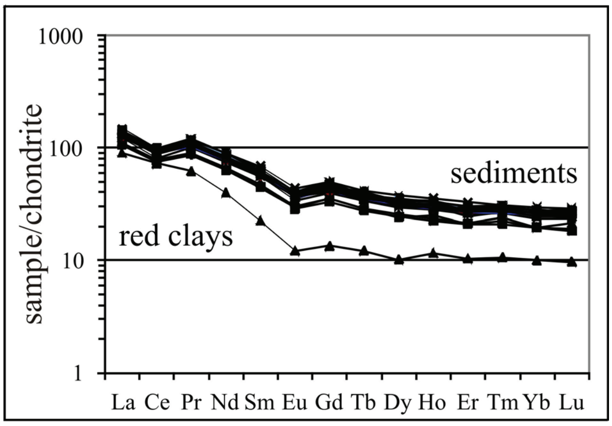

Fig. 1. Chondrite-normalised pattern of REE in the deep-sea sediments, compared to the average "Red clay" of Ziegler et al. (2007)

and mica presented as XRD amorphous phases. There is no identification of organic matter in XRD detectable quantity. Therefore, we can assume that probably authigenic clays and mica of low crystallinity degree are presented. A second halo (22–40° 2θ) was also found that coincides with the area of inorganic XRD amorphous phases, e.g. opal, cristoballite etc.

The samples show high Si, Al, and Ti content, and high Al/(Al+Fe+Mn) and Fe/Mn ratios. The values for characteristic ratios – Fe/(Al+Fe+Mn), (Fe+Mn)/Ti, Al/(Al+Fe+Mn) and (Fe+Mn)/Al – are lower than the required for metalliferous sediments. The chondrite-normalized REE patterns of the samples are very close and exhibit similar features: a negaitive Ce anomaly (Ce/Ce* <1), a negative Eu anomaly (Eu/Eu* <1), and an enrichment of light REE (LREE) relatively to heavy REE (HREE) (La_N/Lu_N >1) (Fig. 1). All samples show nearly flat patterns for HREE distribution. The sum of REY varies between 250 and 325 ppm and refers the sediments to low potential for REY mud according to Kato et al. (2011). The sediments are slightly enriched in REE compared to average "Upper red clay" (Ziegler et al., 2007). NASC (North American Shale Composite, according to Dubinin, 2004) normalized diagram displays again clear negative Ce anomaly, but no Eu anomaly, and a rather middle and heavy rare earth enrichment.

Discussion and Conclusions

Our samples plot in the field of hydrothermal metalliferous sediments on the ternary genetic diagram of Bonatti et al. (1972), so the origin of the sediments could not be identified appropriately based on main ore elements relations. Trace elements data do not support the metalliferous character of the sediments and point out to a conclusion for a polygenetic formation that would be supposed by their mineralogy.

REE distribution patterns of the studied sediments differ from that of the pelagic red clay and show some similarities with that of deep sea-water from the North Pacific. This is a consequence very probably of precipitation of Fe-Mn hydrothermal phases in close contact with seawater and corroborates the common knowledge that the sediments inherit their REE signature from the deep sea-water (Dubinin, 2004). The patterns do not show any distinct positive Eu anomaly that would indicate clear hydrothermal component. Two main factors interplay in the sedimentation processes: a decrease of sedimentation rates, owing to increasing distance from the continent that leads to a relative increase in REE concentration accompanied by decrease in the LREE proportion and appearance of a negative cerium anomaly because of increase of deep seawater influence (Dubinin, 2004). The normal oceanic sedimentation has been probably influenced by volcanic ash/ and hydrothermal activity. The combination of mineralogical and geochemical criteria suggests the oceanic deep-sea sediments studied have complex genetical record reflected on REE distribution.

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