Rare earth elements in core marine sediments of coastal East Malaysia by instrumental neutron activation analysis

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HIGHLIGHTS

- Measurement the REEs distribution in the Malaysian East core marine sediment by INAA.
- Standard reference materials were used as quality control of analytical procedure.
- Assessment the contamination based on EF of related elements to the average shale.
- Shale-normalized used to understand the geochemistry processes in marine sediment.
- The chondrite has been used to understand the natural origin of the REEs.

ARTICLE INFO

ABSTRACT

A study was carried out on the concentration of REEs (Dy, Sm, Eu,Yb, Lu, La and Ce) that are present in the core marine sediments of East Malaysia from three locations at South China Sea and one location each at Sulu Sea and Sulawesi Sea. The sediment samples were collected at a depth of between 49 and 109 m, dried, and crushed to powdery form. The entire core sediments prepared for Instrumental Neutron Activation Analysis (INAA) were weighted approximately 0.0500 g to 0.1000 g for short irradiation and 0.1500 g to 0.2000 g for long irradiation. The samples were irradiated with a thermal neutron flux of $4.0 \times 10^{12}\ cm^{-2}\ s^{-1}$ in a TRIGA Mark II research reactor operated at 750 kW. Blank samples and standard reference materials SL-1 were also irradiated for calibration and quality control purposes. It was found that the concentration of REEs varies in the range from 0.11 to 36.84 mg/kg. The chondrite-normalized REEs for different stations suggest that all the REEs are from similar origins. There was no significant REEs contamination as the enrichment factors normalized for Fe fall in the range of 0.42–2.82.

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1. Introduction

A variety of human activities, e.g. mining, agricultural activities, urban and industrial development, and recreation are potentially causes of metals contamination in living organisms of aquatic systems (Allen, 1993; Cortes et al., 2003; García-Lorenzo et al., 2012; Vaalgamaa and Conley, 2008). Marine sediments in the aquatic ecosystem are analogous to soil in the terrestrial ecosystem as they are the source of nutrients that are the basis of support to living aquatic organisms (Uwah et al., 2013). The natural sources are released due to mobilization of naturally-occurring REEs in the

Earth's crust and mantle, such as volcanic activity and weathering of rocks. Weathering of rocks releases natural elements to soils and aquatic systems, which plays a significant role in the global cycle and enriching the ecosystems with metals (Enell and Wennberg, 1991; Gribble, 1994).

Among the trace metals, REEs have been applied widely to trace geochemical processes and anthropogenic disturbance in natural systems (Jung et al., 2012; Morgan et al., 2012; Prego et al., 2012; Taylor and McLennan, 1985) and have been demonstrated to be powerful tools to characterize the origin of these accumulated elements (Carignan and Gariépy, 1995; Chiarenzelli et al., 2001).

In marine sediments, REEs have been confirmed as a reliable tool for determining depositional processes and sediment provenance, precisely because of their conservative behavior (especially

their immobility in water) during sediment formation (Jung et al., 2012; Taylor and McLennan, 1985).

It is widely recognized that marine ecosystems can become contaminated by trace metals from numerous and diverse natural and anthropogenic sources.

Sediments accumulate natural and anthropogenic products from the overlying water, acting both as a sink or a source of contaminants. Furthermore, marine sediments could act as a non-point source of contaminants causing adverse effects to organisms and to human health through trophic transfer.

Environmental contaminants in marine sediments are emissions of toxic chemicals arise from industrial and municipal discharges of waste water. The runoff from cities, towns and agricultural areas may also contribute to the anthropogenic origin of the REEs in the marine sediments.

Numerous methods have been used for determination of metal concentrations in samples, including Instrumental Neutron Activation Analysis (INAA), Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS) techniques, etc. (Khadijeh et al., 2009). Many studies on the geochemistry of sediments in Malaysia have been reported (Al-Zahrany, 2007; Wood, 2001; Wood et al., 2004). However, there are no baseline data regarding the core marine sediments in the coastal areas of East Malaysia, which is considered the most productive ecosystems and having important economic growth. The concentration of REEs present in the core marine sediments of East Malaysia determined by INAA is described in this paper. INAA has been chosen in this study due to its inherent sensitivity, accuracy, its capability for multi-elemental non-destructive analysis and a lower possibility of contamination in sample preparation (Ashraf, 2011; Ibrahim et al., 2014; Meloni et al., 1987; Wood, 2001).

2. Experimental

2.1. Study area and sampling procedure

Sediment cores were collected from East Malaysia at the five locations shown in Fig. 1. Five core sediments were identified as SB01 (06° 00.0′ N, 115° 00.0′ E), SB02 (06° 32.7′ N, 115° 53.9′E), SB03 (07° 24.68′ N, 116° 46.91′ E), SB04 (05° 49.88′ N, 118° 41.89′ E) and SB05 (04° 44.87′ N, 118° 38.77′ E). The core sediment samples collected at a sea depth of between 49 and 109 m from the South China Sea in the west, the Sulu Sea in the east, and the Sulawesi Sea in the south east of coastal Sabah in East Malaysia using a box

corer of 20 cm × 30 cm cross-sectional area taken to a depth of 60 cm, with the central core cut into strata between 2 and 3 cm intervals. The procedures adopted in the coring activities were documented earlier (Wood, 2001). The sediment core samples were transferred into pre-cleaned vials for future analyses.

2.2. INAA analytical method

The concentrations of REEs in core marine sediments of the coastal areas of East Malaysia were measured using INAA technique for its sensitivity, accuracy and precision. The sediments were dried in the oven for at least two weeks at 60 °C until a constant dry weight was observed. The dried samples were ground using a grinder mill (Herzog) to achieve a homogeneous powdered form approximately < 2 mm mesh size (± 75 μm) (Khadijeh et al., 2009). The powdered sample of each location at different depths was duplicated with approximately 150 mg for short irradiations and 200 mg for long irradiations and were stored separately in heat-sealed polyethylene vials.

The INAA standard comparative method was used for determining the elemental concentrations. The certified IAEA-Soil-7 was used as a multi-element comparator. The certified reference material (CRM) IAEA-Soil-7, standard reference material (SRM) SL-1 (Lake Sediment) and blank samples as calibration and quality control, were irradiated by using a pneumatic transport facility with a thermal neutron flux of 4×10^{12} cm^{-2} s^{-1} at the TRIGA Mark II research reactor operated at 750 kW.

The samples were irradiated for short irradiations for 1 min and counting times of 5 and 20 min after a cooling time of 20 min and 24 h respectively. For long irradiations, the samples were irradiated for six hours and counted for one hour after a cooling time of 3–4 days and 21–28 days respectively.

The Hyper-pure Ge (HPGe) detector and multichannel analyser (MCA) were used for radioactivity counting. The efficiency calibration of the gamma spectroscopy system was carried out by using the standard calibration sources including ^{133}Ba, ^{60}Co, ^{57}Co, ^{137}Cs, ^{54}Mn and ^{241}Am. The distance between the sample and detector was kept at 12–14 cm for short irradiations and 1–2 cm for long irradiations, based on the level of the irradiated samples' activity. The dead time was maintained < 10% in all counting and at the start of counting of the samples (Adazabra et al., 2014; Kumar et al., 2014).

3. Results and discussion

The measured concentrations of various REEs on the core marine sediment samples of East Malaysia for five sampling stations are presented in Table 1. Generally, the vertical distributions of all the measured REE of core marine sediments from the coastal areas of East Malaysia showed similar trends in any given core. The concentration of REE varies by a factor of two to three between different sampling stations of the individual core samples. For LREEs, La concentration ranged between 8.03 mg/kg (at 0–2 cm in station SB03) and 19.60 mg/kg (at 36–38 cm in station SB01); Ce concentration ranged between 16.56 mg/kg (at 24–26 cm in station SB02) and 36.84 mg/kg (at 36–38 cm in station SB01); Eu concentration ranged between 0.31 mg/kg (at 12–14 cm in station SB03) and 0.83 mg/kg (at 36–38 cm in station SB01); Sm concentration ranged between 1.36 mg/kg (at 0–2 cm in station SB03) and 3.87 mg/kg (at 16–18 cm in station SB01). Among the LREE concentration, Sm and Eu showed moderate variation between different cores that varied about by a factor of three at both SB01 and SB03 stations.

For HREE, Dy concentration ranged between 1.71 mg/kg (at 12–14 cm in station SB03) and 3.26 mg/kg (at 0–2 cm in station SB01);
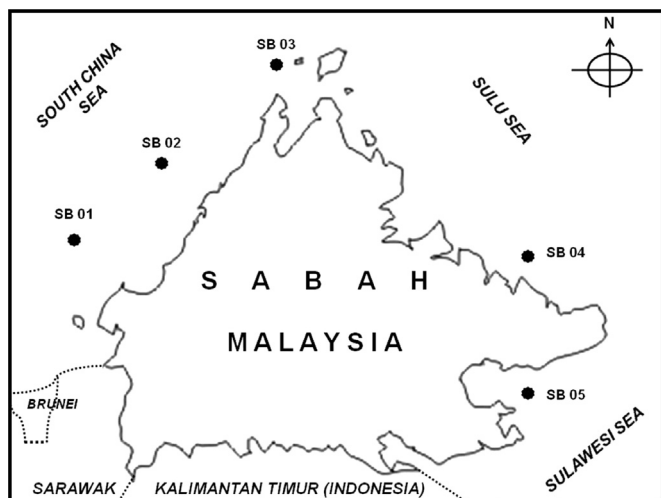

Fig. 1. Map showing location of the sampling stations in the East Malaysia.