

# Rare earth elements, zirconium and hafnium geochemistry in processes of sedimentation and nodule formation in the North-East Pacific

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## Introduction

There are few works dedicated to the geochemical behaviour of zirconium and hafnium in oceanic conditions. At present there are some Zr and Hf determinations in river and sea water and in oceanic sediments and nodules. This study describes geochemical behaviour of REEs, Zr and Hf in the NE Pacific sediments and nodules.

## Methods

Surface sediments and nodules from the trans-Pacific sublatitudinal transect (20°N) from Hawaiian Islands to Mexican coast were used in this study. REE, Zr and Hf determinations were

made by ICP-MS method using PlasmaQuad PQ2+ mass-spectrometer with two internal standards (In, Re) (Dubinin, 1993). Precision for all elements was better than 5%. The accuracy was controlled with standard reference material BCR-1.

## Results and discussion

The sediments of the transect may be divided into the following zones (from east to west): 1) near-shore sediments; 2) hemipelagic sediments; 3) pelagic red clays; 4) muddy siliceous oozes. In terrigenous sediments *LREE/HREE* ratio (where *LREE* = La + Pr + Nd, *HREE* = Er + Tm + Yb + Lu) decreases in the off-shore direction. Relative depletion of *HREEs* in comparison with shale can be resulted from the fact the refractory minerals relatively enriched in *HREEs* loose

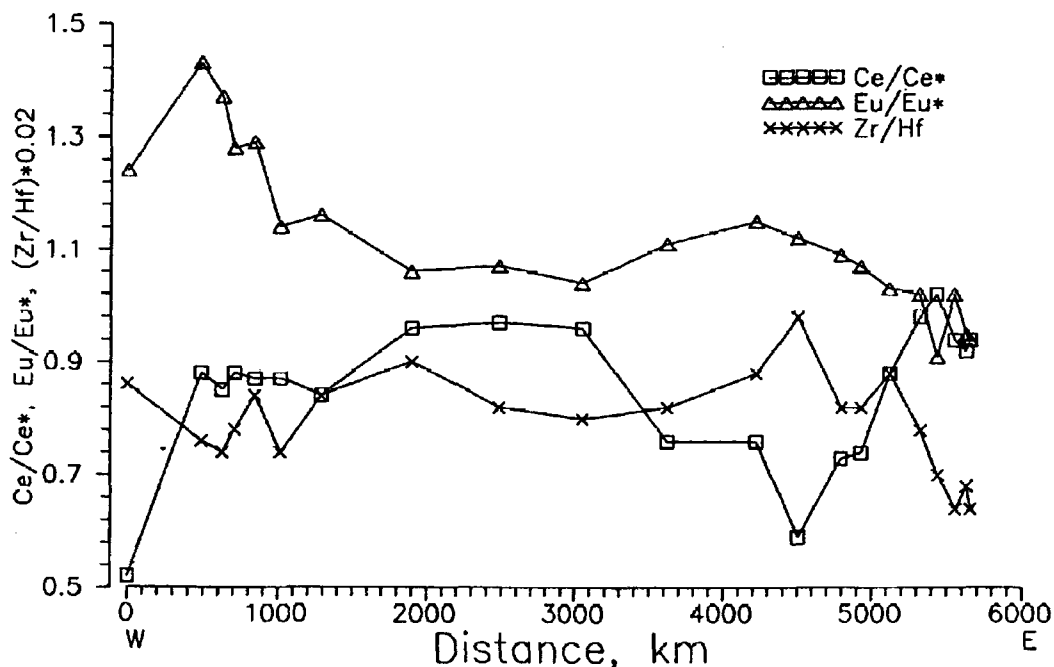


FIG. 1. Ce/Ce\*, Eu/Eu\* and Zr/Hf variations on the transect.

during material transport to the ocean basins. In pelagic area the *REE* pattern shows enrichment in *MREE* relative to shale and reflects increase of hydrogenous input to the sediments. However, pelagic sediments in the six of the nine stations in the area of Clarion Fracture Zone (near EPR) have negative cerium anomaly:  $Ce/Ce^*$  decreases to 0.6 from normal 0.95. The *LREE/HREE* ratio shows similar decreasing. As was shown in previous studies (Fleet, 1984) negative cerium anomaly is a sensitive tracer of hydrothermally originated Fe and Mn oxyhydroxides input. Muddy siliceous oozes with volcanic ash located near Hawaiian Islands have *REE* pattern similar to that of basalts with positive europium anomaly:  $Eu/Eu^* = 1.16-1.43$ . From these data basaltic influence on the sediments can be significant up to 1000 km distance from the source of volcanism (fig. 1).

The Zr/Hf ratio in terrigenous sediments is about 32 (Zr/Hf in shale is 27) and rises to 40–45 in pelagic area. Sediments with minimal Ce

anomaly have Zr/Hf ratio up to 50. In sediments with volcanic ash Zr/Hf ratio varies from 37 to 43 without any trend (Fig. 1). Therefore, Zr and Hf behaviour is unlikely to be influenced by basaltic input because of the similarity of Zr/Hf ratio for basalts and pelagic sediments.

The pelagic nodules have strong positive Ce anomaly:  $Ce/Ce^* = 1.6-2.4$ . By previous studies (Fleet, 1984), this is a hydrogenous origin evidence. High values of Zr/Hf ratio (50–72) is observed in these nodules. As the nodules consist in greater part of hydrogenous material, it is suggested that higher ratio in pelagic sediments than that in shale can be explained by hydrogenous source.

#### References

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