

Distribution of rare-earth elements and yttrium in hydrothermal sedimentary ferromanganese crusts of the Sea of Japan (from phase analysis results)

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Abstract

We have first determined the contents of rare-earth elements and yttrium (REY) in four major mineral fractions of hydrothermal sedimentary ferromanganese crusts of the Sea of Japan. It is shown that REY are sorbed mostly by Fe oxyhydroxides (FeOOH). The REY content in the residual aluminosilicate fraction is the second most important factor determining the crust composition. The manganese fractions, composing more than 80 vol.% of the crusts, plays a subordinate role in REY accumulation. The REY pattern of hydrothermal sedimentary crusts in back-arc basins depicts the sum of the REY contents of the FeOOH fraction (hydrogenous) and residual fractions containing the total REY of the products of bedrock disintegration and endogenous (pyroclastic material) and exogenous (desert dust) components.

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Introduction

Rare-earth elements and yttrium (REY), which is regarded as a geochemical twin of holmium (since they have similar ionic radii (Ho^{3+} —0.901 Å; Y^{3+} —0.900 Å) and electronegativity values (Ho^{3+} —1.10; Y^{3+} —1.11) (Bau and Dulski, 1995)), are a unique group of elements and deserve special attention. This is due, first of all, to the REY property to respond sensitively to changes in the physicochemical conditions of rock formation, which is important for the determination of genesis of geologic objects. To detect the nuances of changes in REY composition during natural processes, it is necessary to exclude the influence of different abundances of REY. This is achieved by normalizing the REY compositions under study to the REY composition in chondrites or shale (Dubinin, 2006).

During their growth (covering tens of millions of years), the ore fractions of ferromanganese crusts sorb a considerable amount of chemical elements from sea water. In addition, metals are substituted and coprecipitate with major oxides.

Correlative relationship of metals with the mineral fractions of crusts is revealed by statistical methods. However, this relationship is statistically difficult to detect for elements concentrated in more than one fraction.

All marine ferromanganese deposits consist of four mineral fractions: I—loosely bound biogenic; II—Mn oxide; III—Fe oxyhydroxide; and IV—residual aluminosilicate (Koschinsky and Halbach, 1995). Intergrown Fe and Mn oxyhydroxides are the main concentrators of sorbed REY (not forming their own minerals (Baturin and Yushina, 2007; Dubinin, 2006)) in oceanic ferromanganese crusts, and biogenic and aluminosilicate fractions play a subordinate role in REY accumulation (Bau and Koschinsky, 2009; Jiang et al., 2011; Mohwinkel et al., 2014; Murdmaa and Skornyakova, 1986; Prakash et al., 2012).

Ferromanganese crusts in the Sea of Japan are assigned to hydrothermal sedimentary deposits according to their mineral and bulk chemical compositions, without separation into authigenic and allothigenic components (Astakhova and Vvedenskaya, 2003; Baturin, 2012; Gershanovich, 1951; Gramm-Osipov and Repechka, 1975; Mikhailik, 2009; Mikhailik et al., 2014, 2015; Pushchin et al., 1975; Shterenberg et al., 1986; Skornyakova et al., 1987). The REY distribution in them, however, indicates positive Ce and negative Y

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anomalies, which are specific to hydrogenous ferromanganese crusts (Mikhailik et al., 2014). In this work we study the REY distribution in different mineral fractions of ferromanganese crusts of the Sea of Japan.

Starting data

The objects of study were 42 samples of ferromanganese crusts dredged from the underwater structures in the Sea of Japan (Fig. 1, Table 1) during the 25th, 29th, and 36th cruises of the “Pervenets” research vessel and during the 16th and 22nd cruises of the “Professor Bogorov” research vessel (Lelikov, 1993) and given to us by E.P. Lelikov and V.T. S’edin (Pacific Oceanological Institute, Vladivostok). The contents of major elements of the mineral fractions (Ca, Mn, Fe, Al, and Si) and REY were a representative sample for revealing correlative relationships by the mathematical statistics method. By now, ferromanganese mineralization in the Sea of Japan has been most comprehensively studied at the Belyaevsky Seamount (Mikhailik et al., 2014). Therefore, three samples of ferromanganese crusts were taken from it for a phase analysis. Samples 2069/2-2 and 2069/2-15-1 were taken from the upper layers of the crusts, and sample

2069/2-P7, from a Mn-ore breccia, which is a “substrate” of layered crusts. In addition, we used data on the REY contents in the basalts from stations 2068 and 2070 to describe the substrate rocks.

Methods

The bulk contents of elements were determined by the gravimetric method (Si), ICP AES (Ca, Fe, Mn, and Al), and ICP MS (REY).

The content of Si in the rocks was determined by the gravimetric method after the decomposition of the sample through its fusion with anhydrous sodium carbonate (Popov and Stolyarova, 1974). The technique of ICP AES (iCAP 6500 Duo (Thermo Electron Scientific, USA)) and ICP MS (Agilent 7700x (Agilent Technologies, Japan)) analyses for major elements and REY in ferromanganese crusts is described in detail by Zarubina et al. (2014). The analytical error did not exceed 5% for Mn and 2% for other elements. The analytical error for REY was no more than 10–15%.

Chemical elements in the mineral fractions of ferromanganese crusts were studied by successive selective leaching (phase analysis) (Chester and Hughes, 1967; Koschinsky and

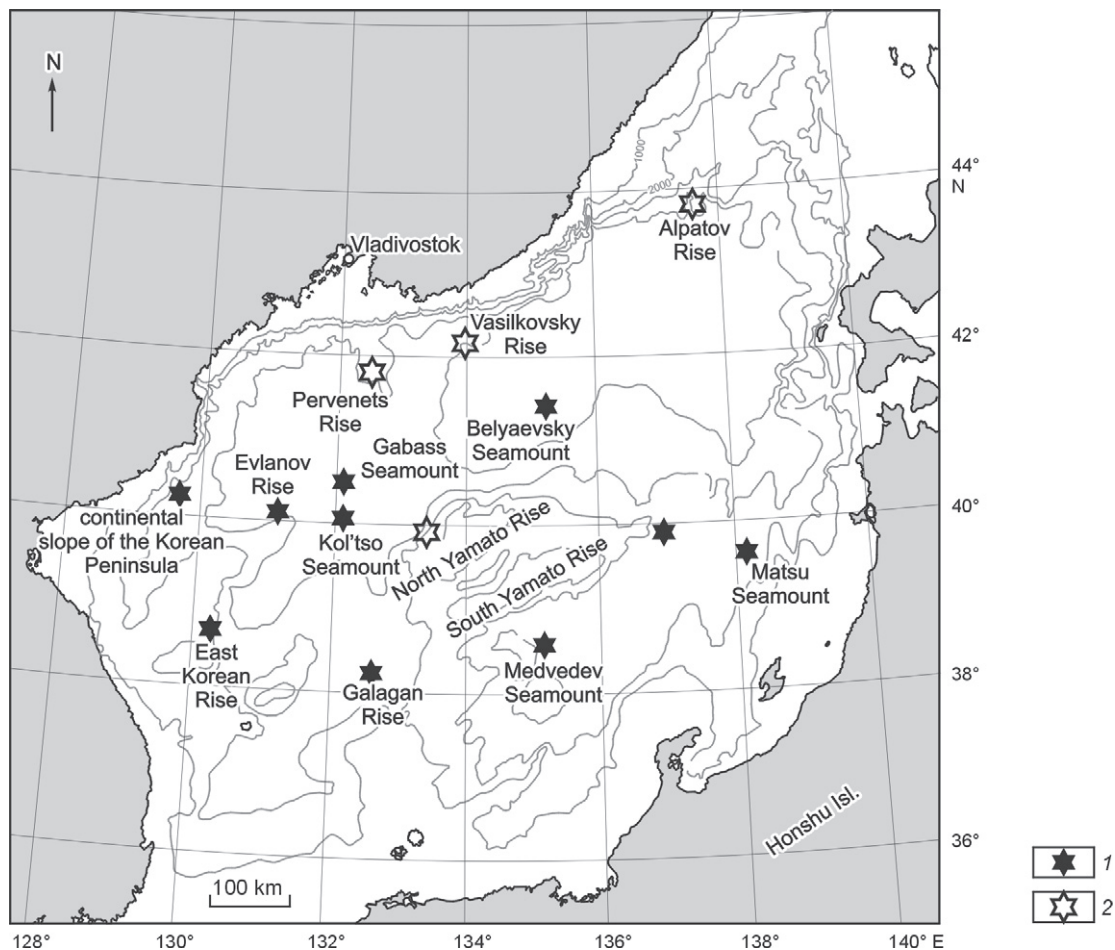


Fig. 1. Distribution of hydrothermal ferromanganese crusts over the bottom of the Sea of Japan. 1, REY contents have been determined; 2, data on REY are absent.

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