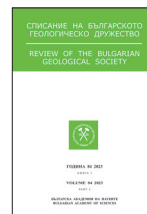




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REE distribution in sequential leached phases from deep-sea polymetallic nodules and sediments

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Разпределение на РЗЕ в последователно селективно екстрахирани фази от дълбокоморски полиметални конкреции и седименти

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Abstract. The distribution of main elements and REE in sequential leached phases from deep-sea polymetallic nodules and sediments from the eastern part of the Clarion-Clipperton fractures zone, NE Pacific are studied. Results show extraction of Mn in the leach 2 in both nodules and sediments. The extraction of Fe, P and REE is different for leach 2, 3 and residual fraction for nodules and sediments. Phosphorous and REE have strong positive correlation which suggests that the phosphate component is the main important carrier of REE in both nodules and sediments but Fe-Mn oxyhydroxides and clay minerals cannot be excluded as carriers of REE.

Keywords: sequential leaching, rare earth elements, polymetallic nodules, deep-sea sediments.

Introduction

Modern society's ambitious goals for a carbon-neutral future are highly dependent on the critical role of raw materials. The deep-sea metalliferous sediments and Fe-Mn polymetallic nodules formed in modern environment at the deep-sea ocean floor (>4000 m depth) were evaluated as promising new raw materials, especially for high-tech elements as Li, Co, Cu, Mn, Ni, and rare earth elements (REE) (Hein et al., 2020). That is why the Clarion-Clipperton Zone (CCZ) in the NE Pacific is the area of greatest economic interest for nodules and sediments extraction (Hein et al., 2020).

In the present study, we use a selective sequential leaching procedure applied by Koschinsky and Halbach (1995) that allows us to separate the major mineral phases of the polymetallic nodules and

sediments and their associated elements with special attention on the REE. Our aim is to reveal the main factors that control the REE concentration in both polymetallic nodules and sediments from the Interoceanmetal (IOM) exploration area located in the eastern part of the CCZ, NE Pacific.

Geological setting and sampling

The studied area covers 630 km² of the seafloor in the eastern part of the CCZ at 4300–4500 m depths. Box-core samples were collected during the 2019 Interoceanmetal cruise. The explored stations were distributed among various morphological types of the bottom relief, represented by undulating hilly plains, intersected by longitudinal ridges and sub-parallel volcanic massifs. The nodules were observed on the top of and partly buried in the sea-

bed sediments. Their main mineral phases are fine-grained, amorphous or poorly crystalline (10°\AA manganate (todorokite), quartz, muscovite, vermiculite). Detrital and authigenic minerals are chlorite, apatite, barite (Hikov et al., 2022a). The nodules are classified as diagenetic and hydrogenetic. The sediment composition down to 45-cm is dominated by light brown siliceous silty clay. The top semiliquid dark brown clay variety (7–12 cm) was denoted as a geochemically active layer. Amorphous or low crystallinity phases (opal, Fe-Mn oxyhydroxides, clays) predominate. Crystalline phases are illite, kaolinite, chlorite, quartz, andesine, cristobalite, barite (Hikov et al., 2022b).

Two nodules and one sediment sample were selected for the leaching procedure. The first nodule (3600N) is diagenetic and contains 32.95 wt % Mn, 5.44 wt % Fe and 760.80 ppm ΣREE while the second nodule (3607N) is hydrogenetic with 22.62 wt % Mn, 8.26 wt % Fe and 380.83 ppm ΣREE (Hikov et al., 2022a). The sediment sample (3600/3-5) is from depth interval 3 to 5 cm and contains 0.70 wt % Mn, 4.36 wt % Fe and 211.15 ppm ΣREE (Hikov et al., 2022b).

Analytical techniques

The bulk samples were separated into four fractions of different mobility and bonding forms (Koschinsky, Halbach, 1995): (1) Easily leachable fraction (extracted by acetic acid/Na acetate buffer, pH 5): exchangeable adsorbed cations and Ca carbonates; (2) Easily reducible fraction (extracted by hydroxylamine hydrochloride buffer, pH 2): Mn oxides; (3) Moderately reducible fraction (extracted by oxalic acid/ammonia oxalate buffer (pH 3.5)): amorphous Fe oxyhydroxides; (4) Residual fraction (total digestion with HF, HCl, HNO_3): crystalline detrital phases (oxides, silica, aluminosilicates). Organic components are negligible in both nodules and sediments.

The chemical analyses of the leached fractions were carried out at the Faculty of Chemistry and Pharmacy, Sofia University using ICP-MS (Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer, following the analytical techniques of Lyubomirova et al. (2020). The concentrations of 69 elements were determined. Standard solutions were prepared from ICP-MS multi-element calibration standard solution-2 (Ultra Scientific) and ICP-MS Multielement Standard B (High Purity Standards).

Results

Relative element distribution in the leaches of the studied samples is shown in Fig. 1. Leaching step 1 for exchangeable adsorbed cations and Ca car-

bonates shows low concentrations for most of the elements, especially for Mn and Fe, because of the lack of Ca carbonates below the critical carbonate compensation depth. The proportion of P is < 1% in nodules and 3% in sediments. The proportions of REE are 2–7% in the nodules and 5–14% in the sediments. Cerium is an exception: it is extracted 0.02–0.06% in nodules and 1% in sediments.

The leach 2 is characterized with complete leaching of Mn in the nodules (97–99%) and sediments (93%). Iron is leached 20–30% in nodules and 11% in sediments. Phosphorous is not leached from nodules but it is leached significantly from sediments (69.6%). The proportions of REE in nodules have similar patterns: the extraction is stronger for La (45–56%), decreases from Ce to Nd (25–28%), increases to Eu (40–52%) and decreases again from Gd to Yb (14–21%). The REE in sediments have opposite pattern: weak extraction for La, Ce, Eu (25–29%) and higher extraction for HREE (41–45%).

The characteristic features of leach 3 are a significant extraction for Fe – 50.33% (3600-N), 24.57% (3607-N), 8.63% (3600/3-5) and mostly complete extraction of P in nodules (95–96%) while in sediments the extraction is only 22%. The extraction of REE is between 38% (La, Eu) and 77% (Yb) for the nodules and between 24% (Eu) and 39–40% (La, Tb, Lu) for the sediments.

The residual fraction is poor of Mn and P (3–6%) while the content of Fe increases from 19% (3600-N) to 80% (sediments). The concentration of REE is between 2 and 11% for nodules. Sediment residue characterizes with higher content of LREE (13–41%) than of HREE (5.7–9%).

The element relations are variegated. Manganese has strong positive correlation (0.7–1) in the leachates with Mg, P, V, Co, Ni, Cu, Zn, Se, Cd, Te, La and moderate (0.5–0.7) with Sr and Eu. Iron has strong positive correlation with Ge and moderate with B, Ti and Cs. Phosphorous has strong positive correlation with Si, Sc, V, Mn, Co, Ni, Cu, Zn, As, Y, Zr, Nb, Mo, all REE, Pb, Bi, U and moderate correlation with Cs, Ta, Hg and W. Most of the REE have strong positive correlation with Si, P, Be, Y, Zr, Nb, Mo, Pb, Bi, U.

Discussion and conclusions

The metal ions and complexes from seawater and sediment pore fluids are sorbed onto the two major host phases, MnO_2 with a negatively charged surface and FeOOH with a positively charged surface (Hein et al., 2020). The 7- \AA and 10- \AA disordered phyllosilicates that compose the diagenetic nodules incorporate metal ions such as Ni^{2+} , Cu^{2+} and Li^+ to balance negative charge deficits in

their crystal lattice. On the other hand, negatively charged complexes of V, Pb, U and REE are attracted by the slightly positively charged FeOOH (Hein et al., 2020).

Our results show extraction differences between polymetallic nodules and sediments. Only Mn is

completely extracted in leach 2 in all studied samples. Iron is preferentially extracted in leach 3 for the diagenetic nodule 3600-N (30% is in leach 2) and prevails in the residual fraction for the hydrogenetic nodule 3707-N and sediments. This feature can be explained by the different origin of the nod-

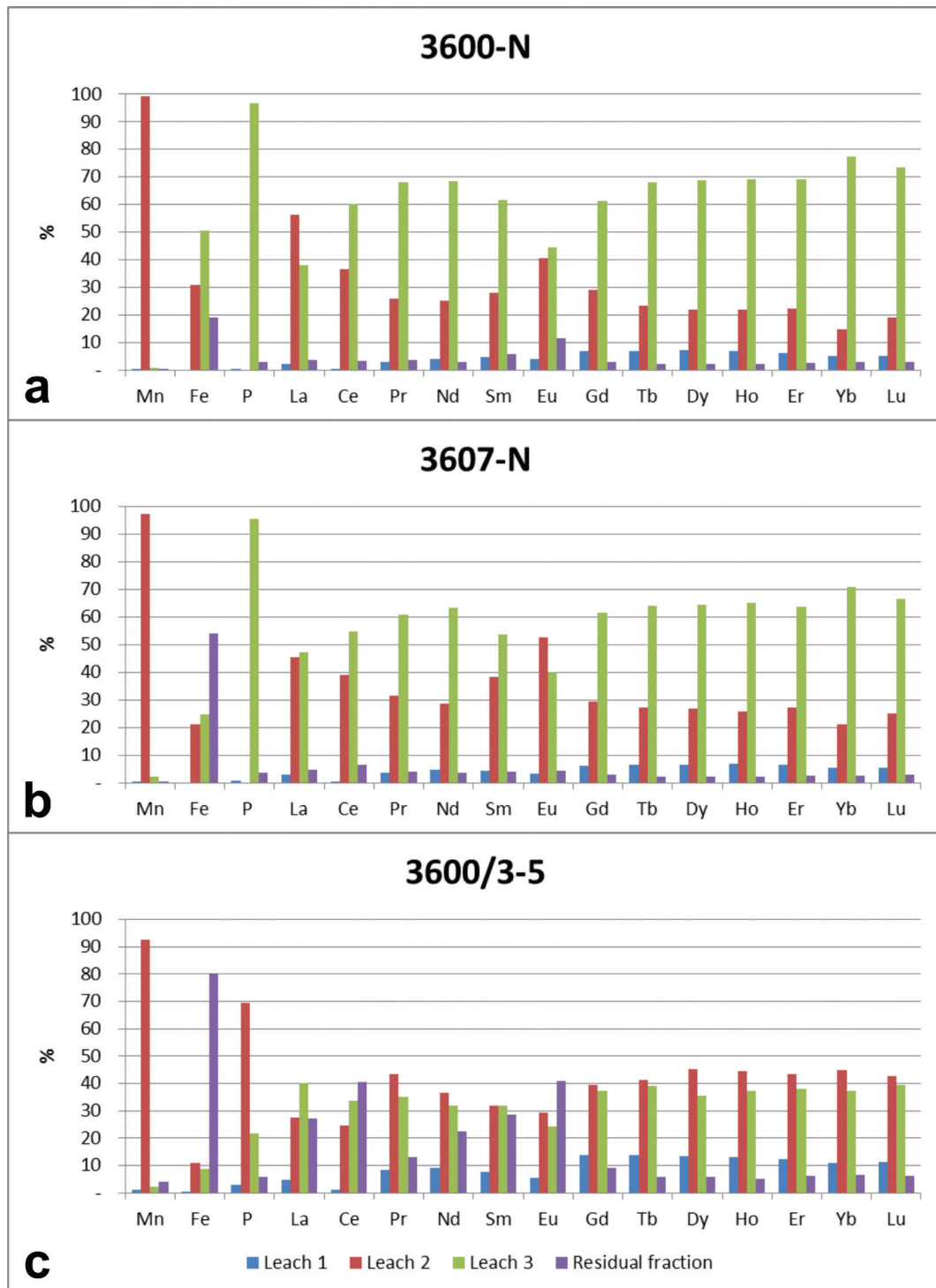


Fig. 1. Relative distribution of Mn, Fe, P and REE in the leaches of two nodule samples: *a*, 3600-N and *b*, 3607-N and one sediment sample: *c*, 3600/3-5 from the IOM exploration area in the eastern part of the CCZ, NE Pacific

ules and by the high amount of detrital sediment material in nodule 3607-N. Partially extraction of Fe in leach 2 attests to that part of Fe is in the form of FeOOH intergrown with the Mn oxide in the vernadite (Koschinsky, Halbach, 1995). Phosphorous is mostly completely extracted from nodules in leach 3, while from sediments it is extracted in leach 2. Koschinsky and Halbach (1995) explain the highest extraction of P in leach 3 with strong association of phosphate to the Fe phase. The extraction of P from sediments in leach 2 and the positive correlation of Mn and P can be a result of an authigenic fine-grained phosphate component (apatite) which is intergrown with the Mn oxyhydroxides.

The correlations found between major and trace elements reflect the mineral composition of the studied nodules and sediments. The first group of elements includes Mn, Co, Ni, Cu, Zn, partly Fe and P. These elements are preferentially incorporated into MnO₂ phases (Hein et al., 2020). The second group of elements (Al, Fe, Ti, K) represents a detrital clay (illite, kaolinite, chlorite) composition and has higher content in the residual fraction. The third group of elements (P, Sc, Y, Zr, Nb, REE, U, etc.) is bound in the authigenic apatite (Li, Schoonmaker, 2014; Menendez et al., 2019). The carriers of REE in deep-sea nodules and sediments include Fe-Mn oxyhydroxides, phosphate components and clay minerals (Dubinin, 2004; Abbott et al., 2019; Hein et al., 2020). The content of REE in the phosphate component is 1–2 orders of magnitude higher than those of the other two carriers (Ren et al., 2021). Our results show that the main important carrier is the phosphate component but the other two carriers cannot be excluded.

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