Trace and REE in micronodules from bottom sediments (Interoceanmetal exploration area, NE Pacific Ocean) determined by in situ LA-ICP-MS

Елементи-следи и REE в микроконкреции от дънни седименти (проучвателна площ на Интерокеанметал, СИ Тихи океан), определени с in situ LA-ICP-MS анализ

Dimitrina Dimitrova[1], Zlatka Milakovska[1], Irena Peytcheva[1], Elitsa Stefanova[1], Valcana Stoyanova[2], Tomasz Abramowski[2]
Димитрина Димитрова[1], Златка Милаковска[1], Ирена Пейчева[1], Елица Стефанова[1], Вълкана Стоянова[2], Томаш Абрамовски[2]

[1] Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria; E-mail: didi@geology.bas.bg
[2] Interoceanmetal (IOM) Joint Organization, 71-541 Szczecin, Poland; E-mail: valcana.stoyanova@iom.gov.pl

Key words: in situ LA-ICP-MS, REY, micronodules, Clarion Clipperton Zone, Pacific Ocean.

Introduction

Previous studies of micronodules have examined the chemical composition by bulk (digested samples) analytical methods. Laser Ablation–Inductively Coupled Plasma–Mass Spectrometry (LA-ICP-MS) in situ analyses provide more detailed information about geochemical characteristics of individual suite of layers within a micronodule and its complicated mechanism of formation.

Geological setting

The Interoceanmetal (IOM) deep-sea exploration area covers 75 000 km^2 in the eastern part of Clarion Clipperton Zone (CCZ), NE Pacific Ocean and is represented by an undulating plain, crossed by a system of longitudinal mid ocean ridges and depressions and sub-parallel volcanic massifs. The Earth's crust in the CCZ has a two-layer composition: sedimentary cover (100–300 m thick, Clipperton and Marquise Formation), and lower part consisted primarily of basalts. The Clipperton Formation is presented predominantly by brown-yellow siliceous silty clays, showing conspicuous bioturbation and containing radiolarian tests, micronodules, macronodules and terrigenous components (Kotlinski, Stoyanova, 2012).

Materials and methods

Bottom sediment samples were provided by IOM from the station 3001 (4457 m depth). The topmost (0–8 cm) layer is composed by homogenous brown clays, of liquid-plastic grading into soft-plastic consistence. It is represented by very coarse silt consisting of radiolarian tests, and clayey aggregates. The underlying layer (8–43 cm) consists of pale-brownish, mottled, soft-plastic clays. Traces of biogenic activity and bioturbation were not found. Micronodules (>63 μm) were handpicked at depth intervals 3–5 cm (S3001-2), 10–15 cm (S3001-5) and 15–20 cm (S3001-6, 7). S3001-5 and S3001-7 micronodules were studied by reflected light microscopy and further by scanning electron microscopy (SEM-EDS) using JEOL-SUPERPROBE 733 SEM equipped with an ORTEC 5000 EDS. A total of 65 elements were determined in situ by LA-ICP-MS using New Wave UP193FX combined with a PerkinElmer ELAN DRC-e ICP-MS at the Geological Institute, BAS. The laser system was operated at constant 8 Hz pulse rate and laser energy was 1.80–2.60 J/cm^2 on the sample surface for 35 μm spot size. External standardization was made on NIST SRM 610, NOD-P-1 and Mass1 standards. Manganese concentrations determined by SEM-EDS were used as an internal standard.

Results and discussion

S3001-5 micronodules have size in the range 250–400 μm, while S3001-7 micronodules – 300–350 μm. All micronodules are mainly red-brown to dark brown, seldom brownish black and usually have irregular rounded, semi-spherical, dendritic, botryoidal, elongated morphology. Their surface texture is fine granular to smooth. The nuclei are rarely distinguishable, represented by Mn-oxyhydroxide particle, biofragment (radiolarian test) or mineral grain. Distinct zoning is observed in most of the micronodules, but layers are either uniform (2–5 μm) near the nucleus or near the edge, or wide and poorly devel-

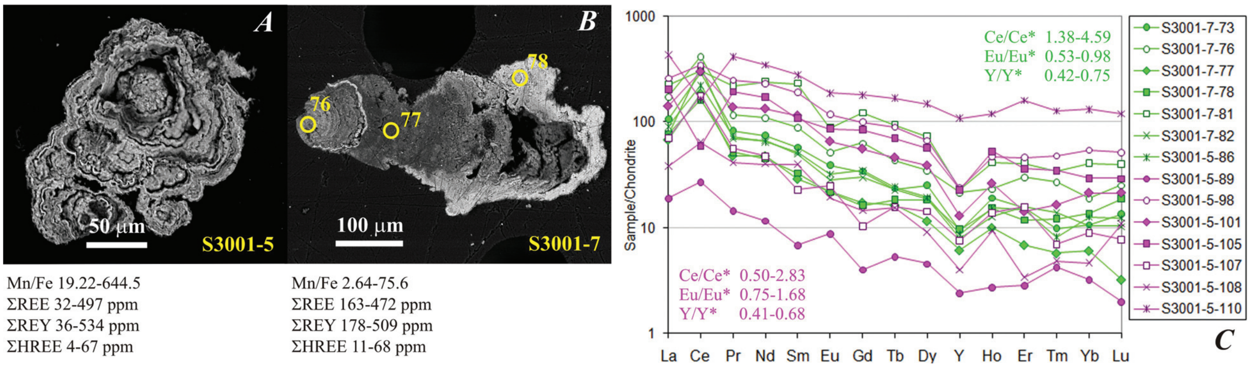

Fig. 1. *A–B*, SEM-BSE images of micronodules; *C*, chondrite-normalized (McDonough, Sun, 1995) REE and Y patterns for micronodule fractions S3001-5 and S3001-7 (in situ analyses 73-110)

oped. Cross sections of micronodules show dendritic segregation. The bands have different mineral and chemical composition visible from SEM-BSE (Fig. 1A–B). Manganese oxyhydroxide phases contain Mn in the range of 11.64–47.46 wt.% and Fe content is 0.02–6.47 wt.%. The ratio of Mn/Fe varies from 2.64 to 644. The lowest Mn/Fe ratio detected in the "core" zone (Fig. 1B, S3001-7-76) could denote hydrogenetic growth as Co and Ti contents are the highest and Ni, Cu and Zn contents are relatively low (Halbach et al., 1981). Increased Mn/Fe ratio and varied higher Ni, Cu and Zn concentrations in the "outer" zone (S3001-7-77, 78 points) suggest diagenetic growth. The "core" zone in this micronodule has higher REE concentrations compared to the "outer" zone. Nickel and Cu concentrations in micronodules (Ni/Cu usually <0.70) are mainly <1 wt.%, suggesting suboxic environment, which sometimes shifts to oxic (Ni, Cu >1.5–2 wt.%). REY (ΣREE+Y) exhibit distinct positive correlations with Fe, P_2O_5, Ti, Zr, Co, while Ni, Cu, Zn correlate positively with Mn. The ΣREE is in the range 32–591 ppm and ΣREY 36–760 ppm (mostly in the range 200–440 ppm – Fig. 1A–B). These values are significantly lower than ΣREE and ΣREY in macronodules from CCZ (Hein et al., 2013). Chondrite-normalized patterns show LREE enrichment and clear positive Ce anomaly (Fig. 1C) in 12 of 14 points. Most of them also have prominent negative Y anomaly. Eu anomaly is faint to weak or is missing. In some points slight enrichment of Er, Tm, Yb is observed.

Conclusions

Existing utilized geochemical classifications (e.g. Halbach et al., 1981; Bau et al., 2014) are based on bulk ICP-MS analyses of nodules and cannot be univocally applied to results obtained by in situ LA-ICP-MS. It points out that every suite of layers within the micronodule reveals specific genetic conditions. S3001-5 micronodules have distinct different REY distribution patterns (positive and negative Ce, faint to negative Y and faint Eu anomalies), while S3001-7 have similar REY patterns (strong positive Ce, negative Y and faint to missing Eu anomalies). The results of in situ LA-ICP-MS analyses show a complex diverse mechanism of micronodule formation.

Acknowledgements: The study was financially supported by Interoceanmetal Joint Organization (IOM), Szczecin, Poland.

References

Bau, M., K. Schmidt, A. Koschinsky, J. Hein, T. Kuhn, A. Usui. 2014. Discriminating between different genetic types of marine ferro-manganese crusts and nodules based on rare earth elements and yttrium. – *Chem. Geology*, *381*, 1–9.

Halbach, P., C. Scherhag, U. Hebisch, V. Marchig. 1981. Geochemical and mineralogical control of different genetic types of deep-sea nodules from the Pacific Ocean. – *Mineral. Deposita*, *16*, 59–84.

Hein, J. R., K. Mitzell, A. Koschinsky, T. A. Conrad. 2013. Deep-ocean mineral deposits as a source of critical metals for high- and green-technology applications: Comparison with land-based resources. – *Ore Geol. Rev.*, *51*, 1–14.

Kotlinski, R., V. Stoyanova. 2012. Nodule coverage, morphology and distribution in the Eastern CCZ. – In: *ISA, Technical Study No 6: Prospector's Guide for Polymetallic Nodule Deposits in the Clarion-Clipperton Fracture Zone*, 34–42.

McDonough, W. F, S. S. Sun. 1995. The composition of the Earth. – *Chem. Geology*, *120*, 223–253.