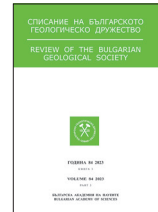




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Trace element characteristics of pore water from the deep-sea sediments of the Interoceanmetal exploration area in the Clarion-Clipperton Fracture Zone, NE Pacific

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Геохимични особености на елементи-следи в порови води от дълбоководните седименти в лицензионната площ на Интерокеанметал в разломната зона Кларион-Клипертон, СИ Тихи океан

Златка Милаковска¹, Атанас Хиков¹, Вълкана Стоянова², Ирена Пейчева¹, Томаш Абрамовски^{2,3}

Abstract. The concentrations of Fe, Mn, Co, Cd, Zn, Cu, Mo, and As were registered in broad intervals and are elevated compared to the mean values for the ocean water. Vertical distributions of the element concentrations in the pore waters along four sediment cores show distinct differences, mainly for the elements Fe, Mn, Cu, and Zn. Bioturbation activities developed in the depth interval 7–15 cm could be a probable reason for the variation trends. The distributions for the elements As, Cd, Co and Zn are conservative type and the patterns for the Mo and Ni – scavenged type. The obtained pore water profiles are similar to the distribution trends for areas in the Eastern Equatorial Pacific and show different patterns from the pore waters from the Western Pacific.

Keywords: trace element characteristics, pore water profiles, deep-sea sediments, Clarion-Clipperton Fracture Zone, NE Pacific.

Importance of the sediment pore water profiles

The interstitial pore waters of the deep-sea sediments contain products and reactants of all early diagenetic reactions that sequester, recycle and release dissolved species. They are an aqueous continuum of the overlying water column (Homoky et al., 2016). The results for the pore water element contents are important geochemical data for three main reasons (Klinkhammer, 1980): (1) Concentrations near the sea-sediment interface allow making

our first direct estimates of the steady-state fluxes of the elements to seawater; (2) Some elements are sensitive indicators of diagenetic processes driven by the organic matter degradation; (3) Understanding the diagenesis of the elements as inferred from pore water chemistry is important for understanding their distributions in the sediments.

In this contribution we present chemical data for trace element contents in pore water extracted from deep-sea sediments from the NE Pacific. We concentrated on those trace elements closely related to the geochemical characteristics of the deep-sea

polymetallic nodules. The main goal of our study is to follow in depth the behavior of Fe, Mn, Co, Cd, Zn, Cu, Mo and As.

Geological position

Interoceanmetal (IOM) exploration area is located in the eastern part of the Clarion-Clipperton Fracture Zone (CCZ) – a region of high density of polymetallic nodule occurrence and, respectively, where most of the International Seabed Authority (ISA) licenses are concentrated. The samples were collected during the IOM-2019 research cruise. Detailed description of the geological position, sedimentary cover, mineralogy and geochemistry of the sediments up to 45 cm depth and pore water REY geochemistry have been published by Milakovska et al. (2022).

Sampling and method of study

The analyzed four stations, are distributed among various geomorphological structures: undulating hilly plains (stations 3607, 3609, 3615), slope of longitudinal ridge oriented in meridional direction (station 3629), and close to volcanic massif (stations 3607 and 3615). All stations sampled are located below the critical carbonate compensation depth. Sampling strategy included: (i) core-box sediment samples collected from depth intervals 0–5 cm, 10–15 cm, 25–30 cm and 35–40 cm from stations of block H 22 of IOM (Fig. 1 in Milakovska et al., 2022); (ii) on-board pore water extraction from the sediments following the recommendations of ISBA/19/LTC/8 to “collect information on metals and other elements of the background water column in the region of resource exploration”. The water extraction and stabilization procedure is described in details by Milakovska et al. (2022).

Pore waters analyses were carried out at the Trace Analysis Laboratory, Faculty of Chemistry and Pharmacy of the University of Sofia “St. Kliment Ohridski” using ICP-MS Apparatus (Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer, following the analytical techniques of Lyubomirova et al. (2020).

Results and discussion

Element concentrations

The concentrations of Fe, Mn, Co, Cd, Zn, Cu, Mo and As were registered in broad intervals (Fig. 1), generally close to, but elevated compared to the mean values for the ocean water. Differences appear for the trends of distribution for Cu, Zn and As at the water-sediment surface, at depth 0–5 cm. Iron concentration in the pore water is in the range

351–1858 µg/l being the highest for stations 3609 and 3607. The content of the next component, Mn, is ranging from 8.8 to 137.8 µg/l. The concentration values for Cd and Cu are highly variable – from 0.47 to 44.9 µg/l. The values for the other trace elements (Ni, Co, Zn, and As) vary in shorter intervals (Fig. 1). There are no element(s) enriched around the water-sediment interface, i.e., in the shallow sediment layer, while Mn and Fe are clearly enriched in the deepest (25–30) layer of the sediments of stations 3615, 3629, and 3607.

Pore water profiles

The results obtained for the elements Fe, Mn, Co, Cd, Zn, Cu, Mo, and As were studied and discussed in the frame of their depth profile trends (Fig. 1). Vertical distributions of the element concentrations in the pore waters along the sediment cores show distinct differences.

The element distribution for Station 3609 shows different trends. The couples Fe-Mn and Zn-Co have maximal concentrations at depth 10–15 cm. Cadmium and Co concentrations remain relatively constant in depth showing conservative type (Li, 1991) of distribution. Ni and Mo show scavenged type as their concentrations decrease from the surface to deep levels.

Station 3629 is interesting by the close As-Co trend of distribution with maximal values for the 10–15 cm level. Opposite is the distribution for the couple Mn-Zn with minimal values for the 10–15 cm level. The values for Fe concentration increase from the surface to deep levels which determine nutrient type of distribution. Copper and Cd concentrations show conservative type of distribution. At that time, the concentrations of Mo and Ni slightly decrease in depth and point to scavenged type of distribution.

The element trends for station 3615 are similar to station 3629 but very different from those for station 3609. Iron, Mn, and partly Zn and Cu have minimal values at the 10–15 cm interval. The depleted values for Fe and Mn compared to the stations 3609 and 3607 could be bound to the highest Eh values and elevated contents of Mn, Co, Cu, Ba and P in the sediments of station 3615 (Milakovska et al., 2021). Cadmium and Mo have maximal concentrations at 10–15 cm interval. Arsenic and Co show conservative type of distributions, and Ni – scavenged type.

The distributions for station 3607 are distinct from the other 3 stations by the four depth intervals sampled giving the possibility to track peculiarities of deeper pore water. Noteworthy are the opposite distributions of Fe, Ni, Mo, and Mn (maximum at 0–5 and 10–15 cm) and Zn (maximum at 25–30 cm). The distributions for the elements As, Cd and Co are close to the conservative type. Copper has maximal

concentration at the deepest level and together with Fe could be related to the nutrient type of distribution at this station. The predominant negative values for the Ce anomaly for most of the water samples (Milakovska et al., 2022) indicate oxygenated seawater. However, for the samples of stations 3609 and 3607 the Ce anomaly is positive and reducing pore waters could be supposed. The latter is an additional reason

for the Fe and Mn elevated content compared to the stations 3615 and 3629.

The geochemical data for pore water from the samples studied shows similar trends for Fe and Mn distribution, as well as for Ni and Cu for pore water from cores taken at three MANOP (Manganese Nodule Program) areas from the Eastern Equatorial Pacific (Klinkhammer, 1980). A difference could be

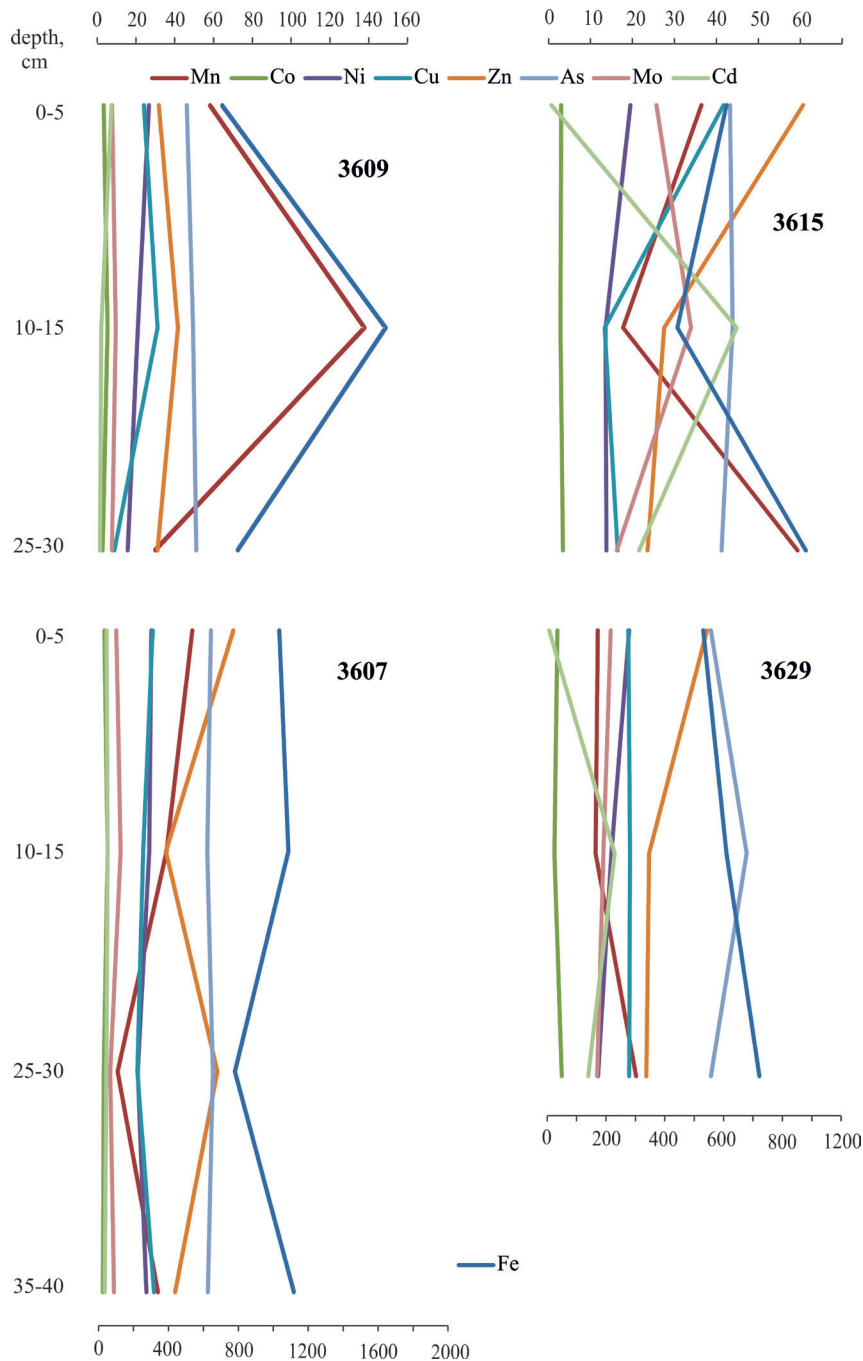


Fig. 1. Vertical distribution of the selected metals (microg/l) in pore waters from stations 3607, 3609, 3615, and 3629 from depth layers: 0–5, 10–15, 25–30 cm. Data for Fe and Mn distribution for station 3607 have been published by Milakovska et al. (2022).

pointed out by the lack of a sharp maximum at the interval 10–15 cm for the MANOP samples but at the deeper level. In contrast to our data, the maximal values for Mn, Cd, Ni, and Co were registered in the interval 0–5 cm for pore waters from Deep-Water Basin, Western Pacific (Deng et al., 2019). Probably the reasons for the distinct element distributions in the different parts of the Pacific Ocean could be traced in the varied depths of the sediment cover below sea level and the diverse depths of Fe and Mn oxidation zone (between 5 and 20 cm) in the sediments.

Conclusion

Our results show that the element concentrations in pore water exhibit a large dynamic range and fractionations connected very probably to the Fe and Mn phases oxidation/reduction. The obtained pore water profiles are similar to the distribution trends in the areas of the Eastern Equatorial Pacific and show different patterns from the pore waters from the Western Pacific. Generally, the element concentration in the pore waters depends on the sediment accumulation rate, the dissolution, reduction and oxidation processes, combined with certain bottom current conditions and diagenetic process (biogeochemistry, adsorption, desorption, transformation and migration). In the case studied, bioturbation activities at the depth interval from 7–8 up to 15 cm (Kotlinski, Stoyanova, 2012) in close relation to the intense polymetallic nodule formation could be assumed as a main reason for trace element relative enrichment/depletion at the different levels in the pore water profiles, in addition to the oxidation state of the elements.

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