Geochemical fractions of heavy metals in bottom sediments of the Pobeda hydrothermal cluster, the Mid-Atlantic Ridge (17◦07′–17◦08′ N)

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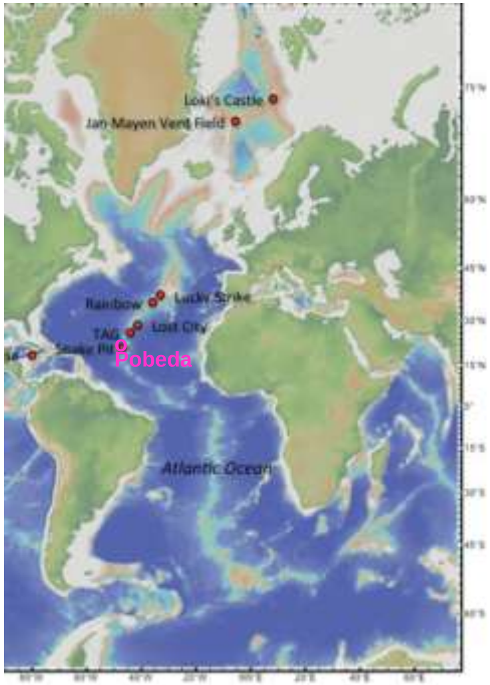

Fig. 1. Scheme of the Pobeda field location at the Mid-Atlantic Ridge.(www.researchgate.net)

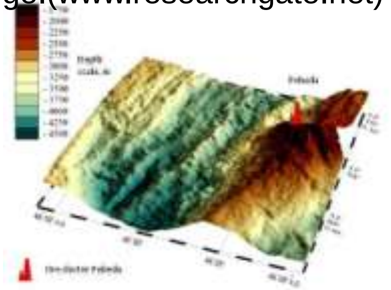

Fig. 2. Scheme of the rift valley and the Pobeda location.

In this work we aimed to evaluate mechanisms of Fe, Mn, Cu, Zn, and Pb accumulation in sediments of the Pobeda hydrothermal cluster, Mid-Atlantic Ridge (Fig. 1). The Pobeda cluster is located on the Eastern wall of the rift valley whose slope is strongly dissected by numerous discharges and cracks (Fig. 2). Position of the massive sulfide ores microphacies changes from the black smoker feeder zone at the base of the ore body (pyrite, wurtzite, isocubanite, sphalerite), to seafloor marcasite-pyrite from diffuser fragments in sulfide breccias [Maslennikov et al., 2020]. Deep rocks are represented by serpentinized and calcined peridotites, serpentinites, gabbroids, serpentine-chlorite rocks, and pyroxenites. The Holocene–upper Pleistocene deposits are carbonate coccolith-foraminiferous bottom sediments, sometimes with admixture of the edaphogenic material and pteropod detritus. In both cores, sediments are enriched in CaCO3 (max 89%) and depleted in organic carbon (Corg ≤ 0.17 %).

We investigated the 70-cm long core of metalliferous carbonate sediments (station 184k, 17^{O} 08.418 'N, depth 2544 m), located In the center of the Pobeda ore cluster, as well as the 110-cm core of background carbonate sediments (St. 215k) located 69 km northwards of the Pobeda (17^{o}44.899‘N, 3535 m depth. Sediment cores were taken with a box-core sampler in an undisturbed state. The mineral composition was examined by the optical and micro-X-ray spectral (SEM TESCAN VEGA 3) and X-ray phase difractometry (D8 ADVANCE Bruker AXS) methods. Geochemical partitioning of Fe, Mn, Cu, and Zn in sediment cores was estimated based on sequential leaching procedure including the following fractions: F-1, exchangeable elements adsorbed mainly onto the clay and carbonate particles, the desorbing solution was acetate buffer [Luoma and Bryan, 1981]; F-2, authigenic Fe-Mn hydroxides and related trace elements, [Chester and Hughes, 1967]; F-3, bound to organic matter and/or sulfides; [Kitano and Fujiyoshi, 1980]; F-4, residual, metals fixed in crystalline lattices (complete acid decomposition with HCl+HNO3+HF). The elemental analysis was performed by the XRF and AAS methods.

Some geochemical and mineralogical features of metalliferous core 184k

Core 184k is composed of foraminiferal-coccolite carbonate biominerals of brown color. Down the core, CaCO3 content reduced from 77 to 20 % (Fig. 3). The Fe total content (carbonate free base, cfb) reached up to 40 %. From the XRD data, the main Fe mineral phase was goethite FeOOH (37–44% on a carbonate-free basis, cfb). XRD analysis identified a rather small quantities (≤ 10-12%) of talc, serpentine, quartz whose total amounts increased down the core reaching up to 50% (cfb). In the sediment core base (depth of 65 cm), Fe-hydroxides make up an essential portion of sediments forming both the finely dispersed and larger isometric particles; the latter resemble pseudomorphoses in foraminifera in shape and size (0.1-0.2 mm) (Fig. 4, 5). At the same time, there are no fragments of the unchanged rocks – feldspars, pyroxenes, and amphiboles.

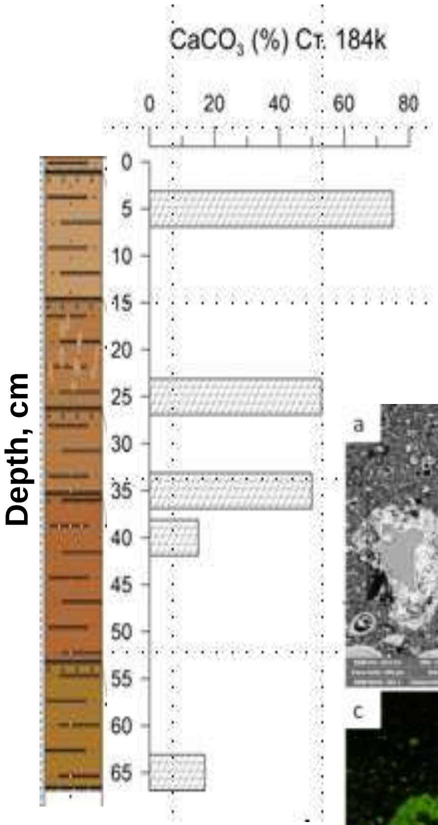

Fig. 3. Lithology and CaCO3 content.

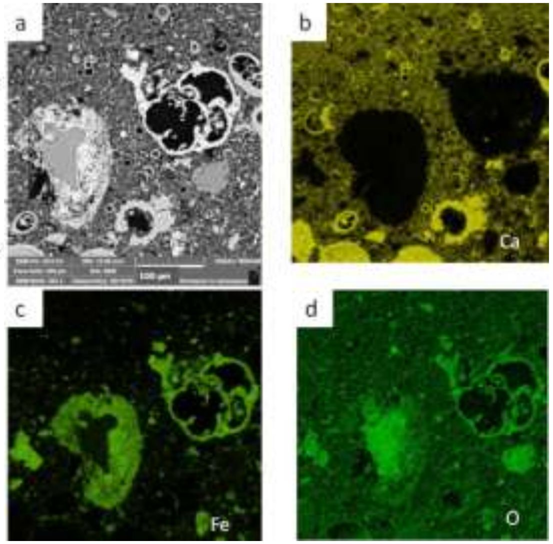

Fig. 4. The SEM images of 38-42 cm sediment layer, core 184k: a – back scattered electrons' images; b − d: maps of the element distribution, b - Ca; c – Fe; d - O.

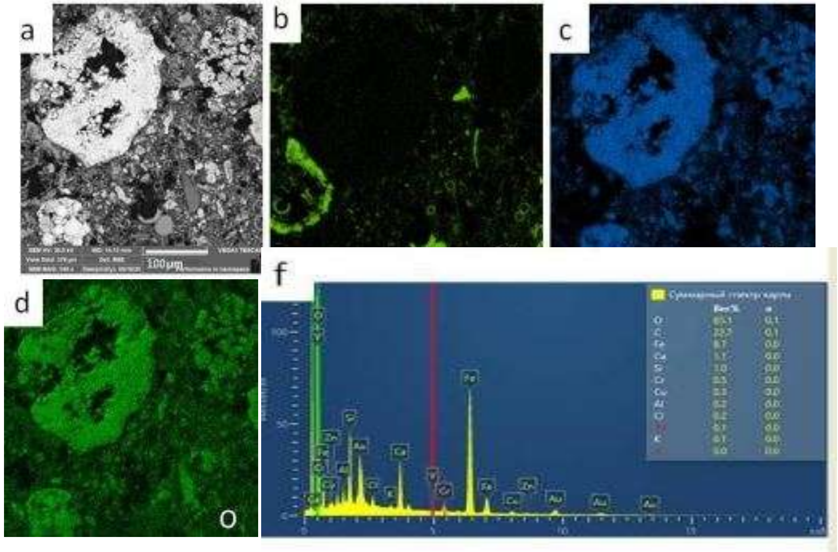

Fig. 5. The SEM images of 65-70 cm sediment layer, core 184k: a –back scattered electrons images; b − d: maps of the element distribution, b - Ca; c – Fe; d – O; f - total X-ray spectrum.

From these data, we might suggest a substitution of the formanifera' tests with the Fe oxy-hydroxides, mainly goethite.

Some geochemical and mineralogical features of the background core 215k

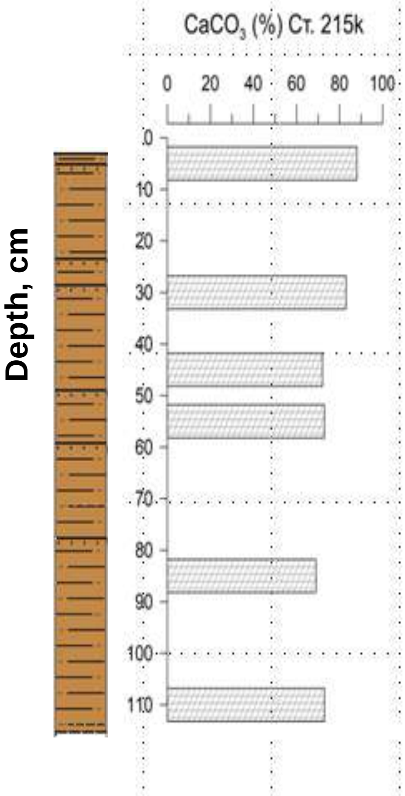

Fig. 6. Lithology
and CaCO3 content.
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The major portion of sediment is presented by biogenic calcite, with the CaCO3 maximal content of 89% (Fig.6).
According to the XRD analysis data, in this core, the terrigenous and edaphogenic minerals: albite, potassium feldspar, pyroxenes, amphiboles, quartz, talc, serpentine, chlorite, palygorskite were detected, as well as an admixture of ore minerals-pyrite and goethite (table).
Clay minerals are represented by kaolinite, illite, smectite.

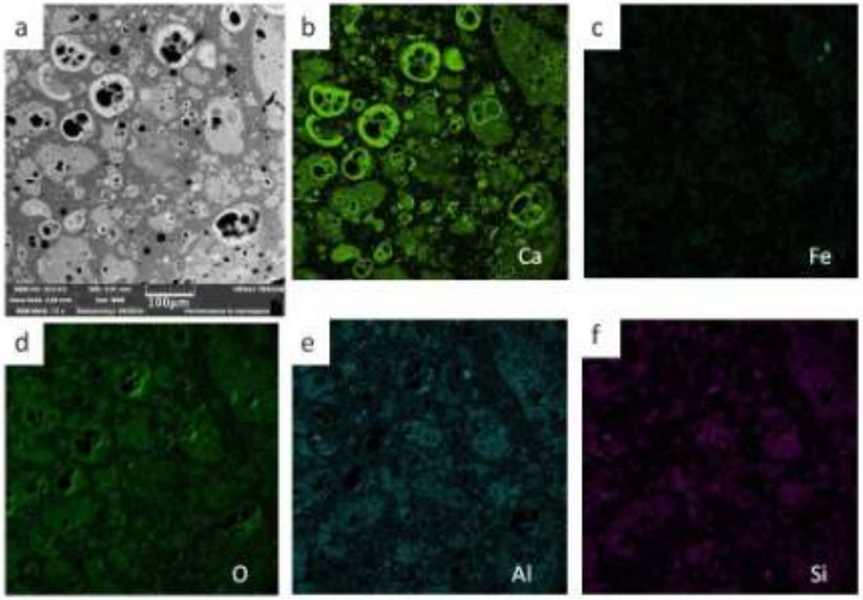
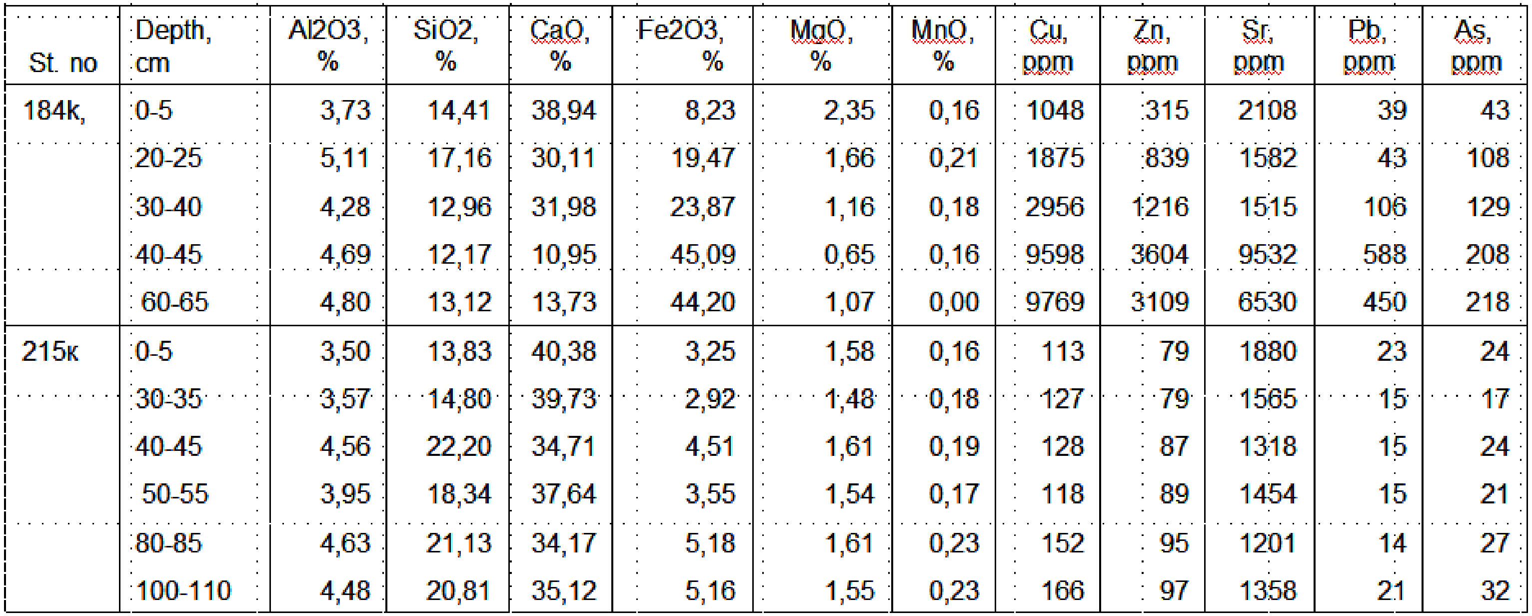


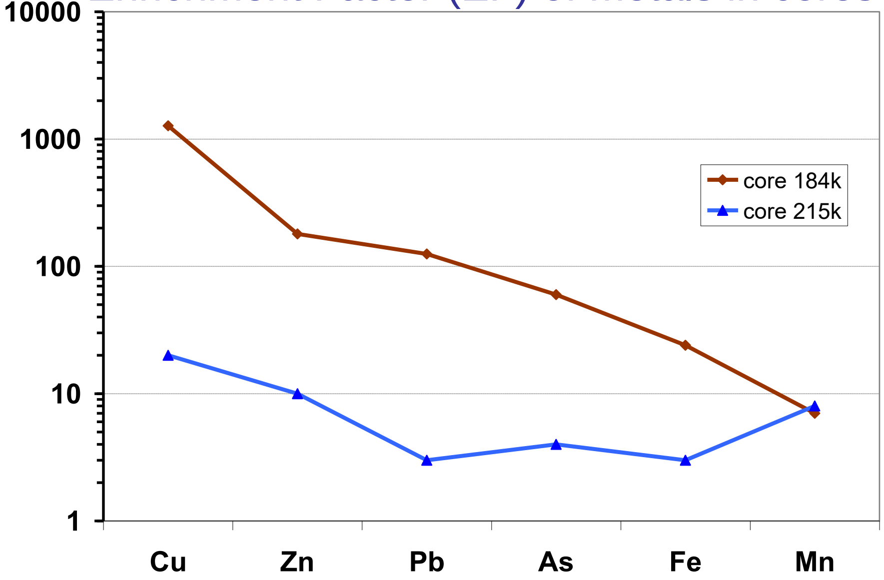
Fig. 7. SEM images of the 100-110 cm sediment layer, core 215k; a – back scattered electrons' images; b − e – maps of elements' distribution: b-Ca, c-Fe, d-O, e - Al, f –Si. Dark areas are the epoxy resin cementing fragments of clay-carbonate sediment with microfossils.

Table. Elements' contents (XRF) in the bulk sediments of metalliferous (St. 184k) and background (St. 215k) cores



St. no	Depth, cm	Al2O3, %	SiO2, %	CaO, %	Fe2O3, %	MgO, %	MnO, %	Cu, ppm	Zn, ppm	Sr, ppm	Pb, ppm	As, ppm
184k,	0-5	3,73	14,41	38,94	8,23	2,35	0,16	1048	315	2108	39	43
	20-25	5,11	17,16	30,11	19,47	1,66	0,21	1875	839	1582	43	108
	30-40	4,28	12,96	31,98	23,87	1,16	0,18	2956	1216	1515	106	129
	40-45	4,69	12,17	10,95	45,09	0,65	0,16	9598	3604	9532	588	208
	60-65	4,80	13,12	13,73	44,20	1,07	0,00	9769	3109	6530	450	218
215к	0-5	3,50	13,83	40,38	3,25	1,58	0,16	113	79	1880	23	24
	30-35	3,57	14,80	39,73	2,92	1,48	0,18	127	79	1565	15	17
	40-45	4,56	22,20	34,71	4,51	1,61	0,19	128	87	1318	15	24
	50-55	3,95	18,34	37,64	3,55	1,54	0,17	118	89	1454	15	21
	80-85	4,63	21,13	34,17	5,18	1,61	0,23	152	95	1201	14	27
	100-110	4,48	20,81	35,12	5,16	1,55	0,23	166	97	1358	21	32

Enrichment Factor (EF) of metals in cores



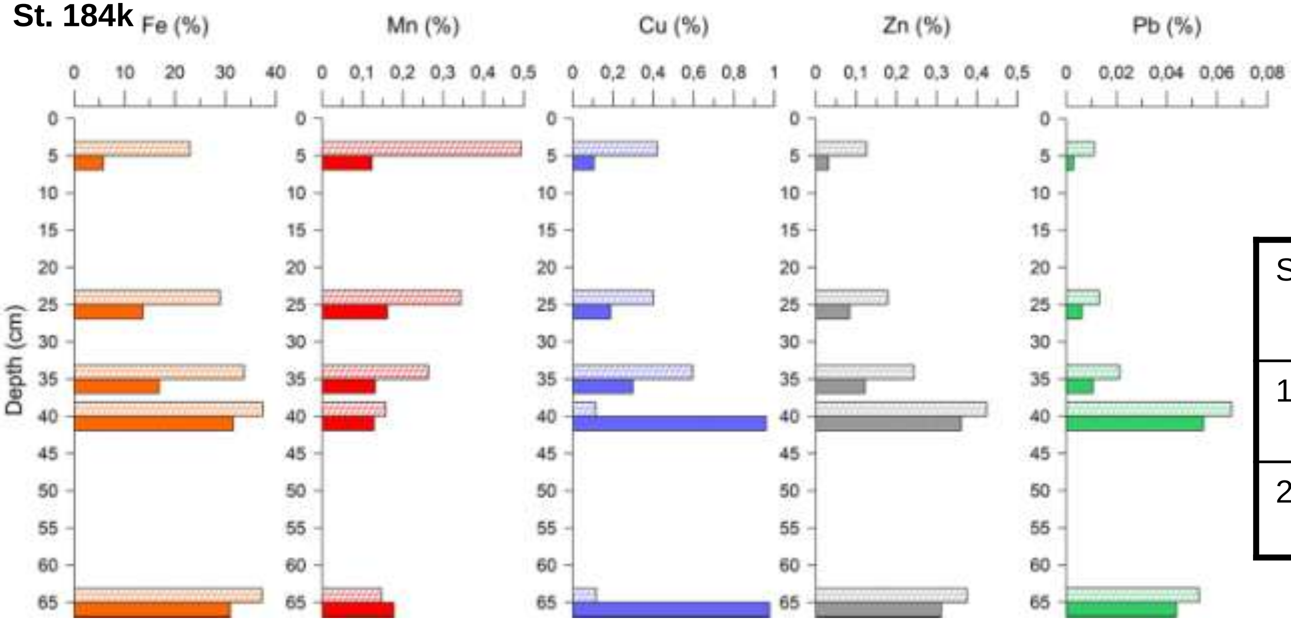
EF =(El/Al)sample/(El/Al)UCC [Rudnick, Gao, 2004].

In metalliferous core 184k, Enrichment Factor of metals varied from 8 (Mn) to 1100 (Cu). Comparison of both the cores revealed that Mn is the only metal whose EF value for metalliferous sediments didn't exceed EF for background sediments.

Down-core metal distribution in metalliferous (St.184k) and background (St. 215k) sediments

Metal content in bulk sediment is shown with dense fill; while that calculated on the carbonate free basis (cfb)– fill with hatching.

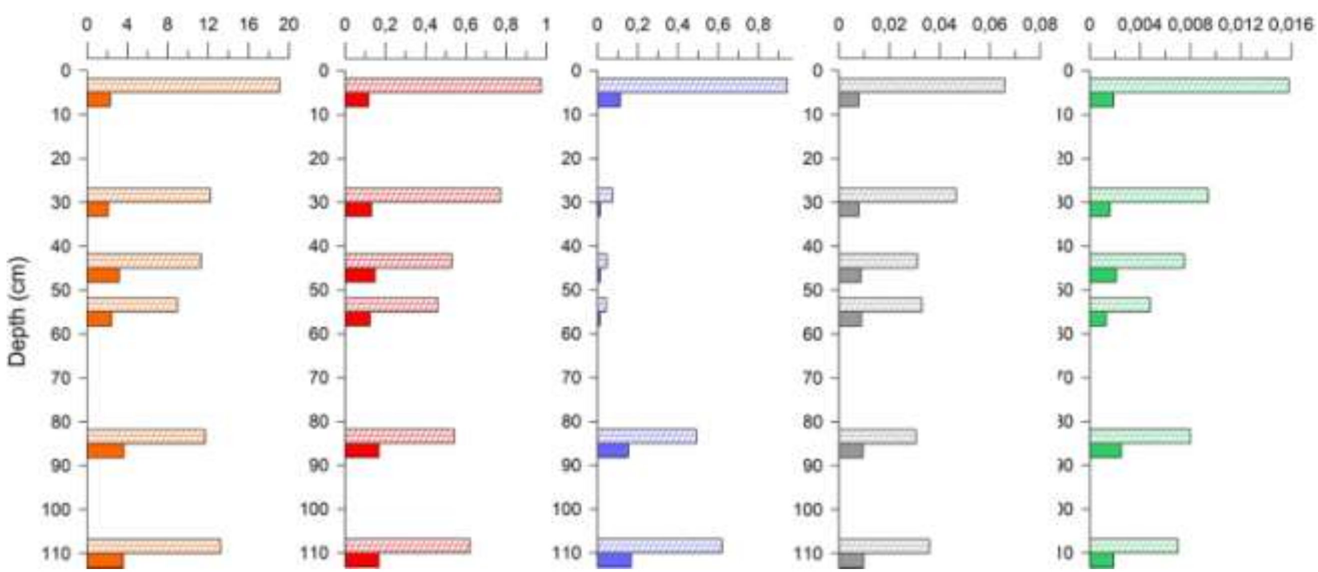
St. 184k



Average metal content, cfb;
Fe, Mn - %,Cu, Zn, and Pb –ppm.

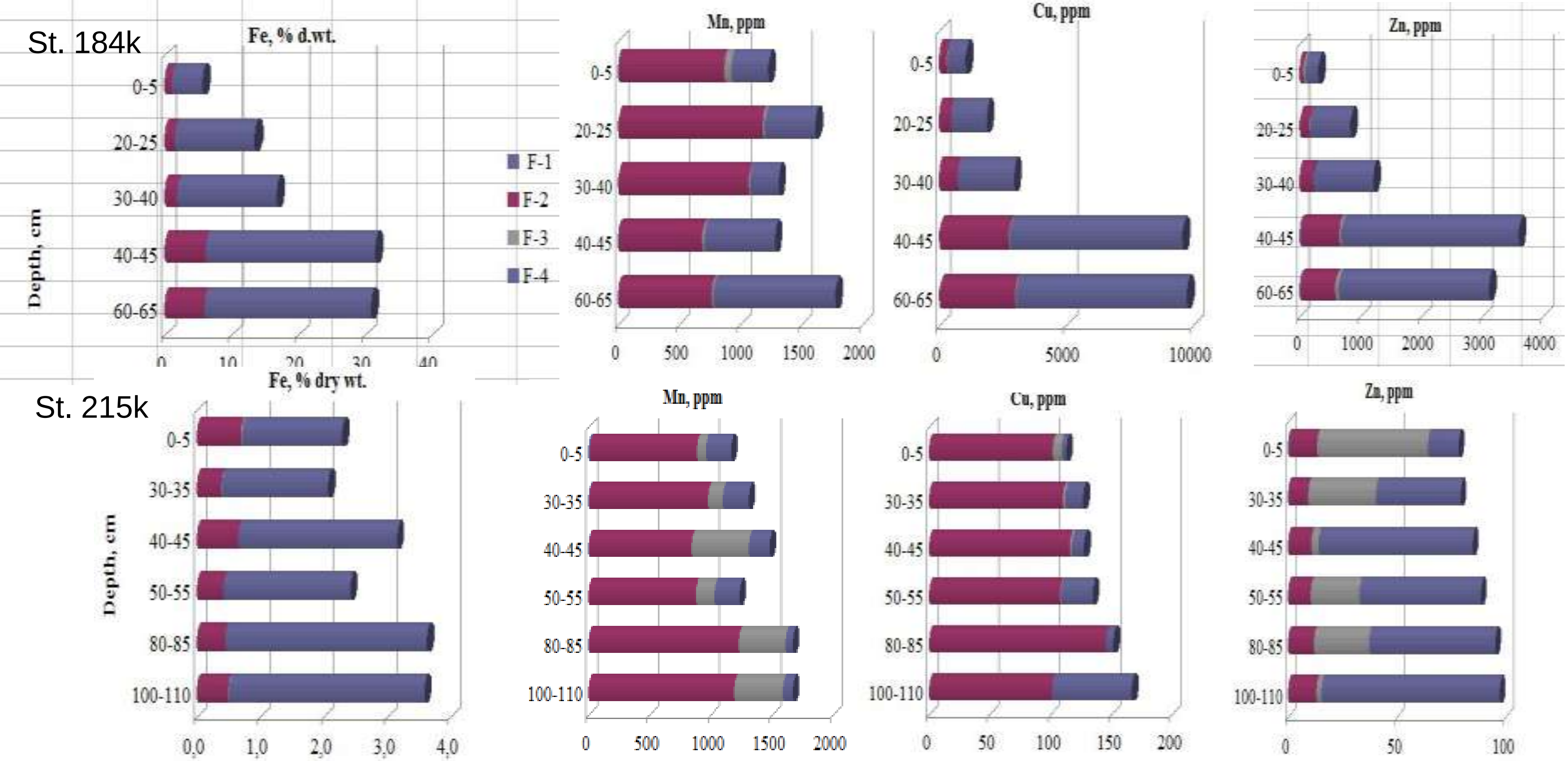
St.	Fe	Mn	Cu	Zn	Pb
184k	32.1	0.28	0.74	0.27	0.033
215k	12.7	0.65	0.37	0.04	0.009

St. 215k



From these drawings, one can see that biogenic carbonate has a diluting effect on the metal contents in both the cores.

Geochemical fractions of metals in the metalliferous (St.184k) and background (St. 215k) cores

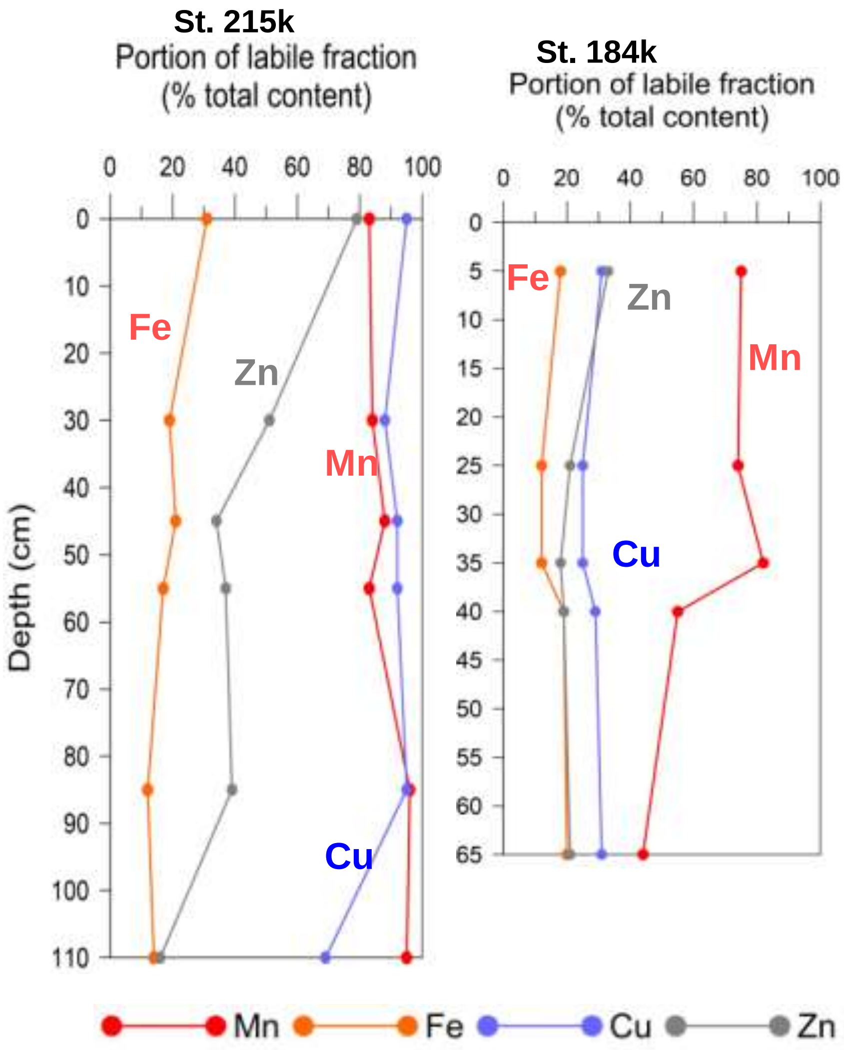


Fractions: F-1, exchangeable elements adsorbed mainly onto the clay and carbonate particles; F-2, authigenic Fe-Mn hydroxides and related trace elements; F-3, bound to sulfides; F-4, residual, metals fixed in crystalline lattices

In both cores, the main mass of Fe (up to 70% of total content) was represented by the residual fraction. Among geochemically mobile fractions (F-1, F-2, and F-3), 90 to 97% of total Fe was detected in the form of authigenic oxyhydroxides (F-2). The same fraction was the predominant host for Mn in both metalliferous and background sediments (55-85%). 40-96 % of Cd, Cu, Zn, and Pb were associated with these Fe and Mn fractions. The sulfide fraction did not exceed 10% of majority of metals, with the exception of Zn and Mn in the background core where its portion reached up to 50% of their total content.

In metalliferous sediment core 184k, the maximum concentrations of metals and their geochemically mobile fractions were recorded in the deeper layers, an observation that might be attributed to influence of hydrothermal diffused fluids.

Down-core distribution of the sum (F-1 + F-2 + F-3) labile fractions in the metalliferous (St. 184k) and background (St. 215k) sediments



The sum of labile fractions (F-1, F-2, and F-3) of heavy metals represents a portion of each metal that could be accumulated by the bottom fauna.

Comparing two cores one can see that in the background sediments (st. 215k), percentage of bioavailable forms of heavy metals Zn and Cu was 2 to 3 times higher than that in metalliferous core 184k. Thus, in the latter we might suppose a reduced level of the potentially toxic Zn and Cu bioaccumulation that seems to be more favorable for bottom organisms. At the same time, a percentage of the Fe and Mn bioavailable fractions doesn't differ significantly between two sediment cores.

Conclusions

The main mass of Fe (up to 70% of total content) was represented by the lithogenic fraction; among geochemically mobile fractions, 90-97% of total Fe was found in the form of authigenic oxyhydroxides. The same fraction was the predominant host for Mn in both metalliferous and background sediments (55-85%). 40-96 % of Cd, Cu, Zn, and Pb were associated with these Fe and Mn fractions. The sulfide fraction amounted to roughly 10% for majority of metal. In metalliferous sediment core 184k, the CaCO3 content decreases from 77% to 20% down the core due to its substitution with authigenic goethite, on the one side, and an increase in the number of modified ultrabasites fragments, on the other side.

The maximum concentrations of metals and their geochemically mobile fractions were recorded in deeper layers, an observation that might be attributed to influence of hydrothermal diffused fluids and fragments of transformed rocks. Our data suggested that metals were mostly accumulated in carbonate sediments in their contact zone with the underlying serpentinized periditites. These data indicate a significant influence of tectonic and hydrothermal processes on carbonate deposits in zone of their contact with the bed rocks [Gablina et al., 2021, in press].

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References

Chester, R., Hughes, M.J., 1967. A chemical technique for separation of ferromanganese minerals and adsorbed trace metals from pelagic sediments. Chemical Geology 3, 249–262.

Gablina I.F., Dobretsova I.G., Popova E.A., Dara O.M., Sadchikova T.A., Gorkova N.V.,Mikheev V.V., Mineral composition and geochemical zonality of the Pobeda hydrothermal field (17°07–17°08 N, Mid-Atlantic Ridge) // Lithology and mineral resources. 2021, accepted, in press.

Kitano, Y., Fujiyoshi, R., 1980. Selective chemical leaching of Cd, Cu, Mn and Fe in marine sediments. Geochemistry Journal 14, 122–128.

Luoma, S.N., Bryan, G.W., 1981. A statistical assessment of the forms of trace metals in oxidized estuarine sediments employing chemical extractants. Science of the Total Environment 17, 165–196.

Maslennikov V.V., Cherkashov G.A., Artemyev D.A., Firstova A., R. Large R.R. Tseluyko A., Kotlyarov V. Pyrite Varieties at Pobeda Hydrothermal Fields, Mid-Atlantic Ridge 17o07–17o08 N: LA-ICP-MS Data Deciphering. Minerals. 2020. 10, 622; doi:10.3390/min10070622

Rudnick, R. L., Gao, S., 2003. Composition of the continental crust. Treatise on Geochemistry 3, 1–64.

Thank you for attention!