

Variability in Contents of the Major Ore Components of Ferromanganese Formations in the Lakes–Seas–Oceans Series

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Abstract—Based on statistical methods, the available literature data were processed to analyze regularities in the distribution of five ore elements (Fe, Mn, Cu, Co, Ni) in ferromanganese nodules and crusts in an idealized lakes–seas–oceans profile. Application of the cluster analysis confirmed the regularities revealed by calculations of the mean contents of these elements and unraveled some additional features of their distribution.

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INTRODUCTION

Ferromanganese nodules and crusts (FMNC) are particularly widespread in oceans, but they are also known in seas, lakes, artificial ponds, rivers, bogs, and soils. High interest to such formations is caused by their ore potential. In this connection, oceanic nodules, which can serve as resource of Co, Ni, Cu, Mo, and Mn, are most interesting.

Several decades of the study of such ferromanganese formations promoted the gathering of large information concerning the composition, genesis, growth rate, and morphology, as well as other properties and specific features. The overwhelming majority of such studies, however, are devoted to oceans, because they accommodate the major part of ore reserves.

One of the main characteristics of FMNC is the chemical composition, which is developed under the influence of material sources, nodule formation rates and mechanisms, as well as specific physicochemical and hydrological settings. The natural question that arises is whether there are general regularities in the concentration of chemical elements in FMNC from basins of different types; i.e. whether contents of elements change within an idealized lakes–seas–oceans profile. It is noteworthy that contents of chemical (first of all, ore) elements in FMNC show a wide variation range. The Mn content in them varies from a few tenths of percent to 50–60%, while contents of Cu, Ni, and Co can differ by two or three orders of magnitude even in samples taken immediately near each other. Therefore, studies of specific features in the distribution of concentrations of ore elements in FMNC need the application of statistical methods that make it possible to unravel regularities in large digital databases.

The genesis of FMNC remains a debatable issue. Researchers have proposed the hydrogenic, diagenetic, sedimentary-diagenetic, exhalative-hydrothermal, halmyrolytic, and microbiological concepts of their origin. It is quite possible that all these concepts or some of them are correct, and such nodules and crusts are polygenous formations. Explicit distinctions between the existing hypotheses are lacking, and virtually all of the proposed models use some elements of other or synchronously existing genetic concepts. However, no matter what the formation mechanism of these nodules and crusts, their origin in each specific setting requires a sufficient amount of ore material (i.e., mass of Fe, Mn, Cu, Ni, and Co) and favorable conditions for its concentrations.

It is evident that the main source of material for FMNC is represented by the Earth's interior (first of all, hydrothermal solutions) and the discharge of material from land (primarily, river runoff). According to estimates made by Yu.A. Bogdanov, A.Yu. Lein, and A.P. Lisitzyn (Bogdanov et al., 2015), contribution of the endogenic material into the oceanic crust in processes of sedimentation is generally close to that of the material from the continental crust and even higher for some elements. However, precise quantitative relationships between these sources can hardly be estimated convincingly at present.

The aim of our paper is to compile a representative group of FMNC samples furnished with the data on Fe, Mn, Co, Ni, and Cu contents and their statistical processing to unravel regularities in their distribution in FMNC along an idealized lakes–seas–oceans profile. Choice of these five elements was stipulated by the fact that precisely they play a crucial role in the composition and specific properties of FMNC. Therefore, they are of practical interest from the viewpoint of the

extraction and utilization of elements mentioned above. In addition, the majority of publications present data on precisely these elements, making it possible to compile a sufficiently large database.

MATERIALS AND METHODS

Analysis of the available literature made it possible to compile a database composed of 1582 samples. The lacustrine FMNC are represented by 102 samples taken from lakes in Canada, United States, England, Scotland, Sweden, and Russia (Callender, 1973; Calvert and Price, 1970; Edgington and Callender, 1970; Gorham and Swain, 1965; Harriss and Troup, 1969, 1970; Ljunggren, 1955; Rossmann and Callender, 1968; Schoettle and Friedman, 1971; Shcherbov and Strakhovenko, 2004; Strakhov et al., 1968). Among them, 115 samples were taken from the Baltic, Black, Barents, Kara, Okhotsk, Chukot, and Japan seas (Anufriev et al., 2005; Astakhova and Sattarova, 2005; Astakhova and Vvedenskaya, 2003; Astakhova et al., 2010; Baturin, 1987; Baturin et al., 1988; Boström et al., 1982; Georgescu and Lupan, 1971; Gurevich and Yakovlev, 1993; Ingri, 1985a, 1985b; *Kalamitskoe ...*, 1973; Kalinenko and Pavlidis, 1982; Kolesnik and Kolesnik, 2015; Mikhailik et al., 2009; Shnyukov et al., 1991; Trokowitz, 1998; Varentsov et al., 1977; Volkov and Sevast'yanov, 1968). The maximum number of samples (1365) is represented by the oceanic FMNC, with the Atlantic Ocean accounting for 284 samples (Bazilevskaya, 2007; Cronan, 1979; Emel'yanov and Safronov, 1988; Pushcharovskii et al., 2011), the Indian Ocean accounting for 178 samples (Cronan, 1979; Pattan and Parthiban, 2007, 2011; Perritt and Watkeys, 2007), and the Pacific Ocean accounting for 903 samples (Ahrens et al., 1967; Bonatti and Joensuu, 1966; Burns and Fuerstenau, 1966; Cronan and Tooms, 1969; Glasby, 1972; Goldberg, 1954; Grant, 1967; Hewett et al., 1963; Mearou, 1969; Ostwald and Frazer, 1973; Skornyakova and Andrushchenko, 1970; Skornyakova et al., 1962; Strakhov et al., 1968; Summerhayes, 1967; *Zhelezo-margantsevye ...*, 1976).

Materials of this database were used to compute the mean contents of chemical elements, variation coefficients, and pair correlation functions of Fe, Mn, Co, Ni, and Cu for FMNC samples from lakes, seas, and oceans (Table 1, Fig. 1).

Results of these calculations reflect the behavior of chemical elements in an idealized lakes—seas—oceans profile, i.e., from small to large basins. The most significant (in area and depth) Pacific Ocean is the terminal member in this series. The Indian and Atlantic oceans are similar in area. However, because of an isometric shape and greater depths, the Indian Ocean is likely more similar to the Pacific Ocean in this conditional series, whereas the Atlantic Ocean is similar to marginal seas because of an extended shape and lesser

development of the pelagic facies zones with a low sedimentation rate.

It is known that computations of mean arithmetic values can yield unreliable results, for example, if the distribution is bimodal and the sampling comprises actually two groups of samples with appreciably different contents of chemical elements. Such a situation can also arise if the sampling group includes samples with anomalously high or low contents of elements, i.e., the law of distribution does not follow the normal type. As is seen from estimates of the asymmetry and excess (Table 1), the distribution of Cu, Ni, and Co contents in FMNC not always obeys the normal law. Hence, estimates of mean contents can also differ from the real values.

To check the correctness of conclusions about regularities in variations of the mean contents and values of the dispersion of contents of chemical elements in the idealized lakes—seas—oceans profile, the starting FMNC sampling should be divided into groups with the closest chemical composition. This can be achieved with the cluster analysis, i.e., multidimensional statistical procedure regulating objects into relatively homogeneous groups (clusters).

Coincidence of sample groups obtained by the cluster analysis with groups based on basin types will testify that the obtained values of mean contents and variation coefficients depend really on the basin type, i.e., change regularly in the series: lakes—seas—oceans.

The cluster analysis can be accomplished by various methods. At the first approximation, they are divided into hierarchical and nonhierarchical groups. The hierarchical clusterization leads to the successive combination of smaller clusters into large ones (agglomerative methods) or the discrimination of large clusters into smaller ones (divisive methods). With each clusterization step, the number of clusters increases by 1, i.e., from 1 to n (divisive methods) or decreases by 1, i.e., from n to 1 (agglomerative methods). The results of such analysis are illustrated well by the dendrogram or cluster diagram.

Among nonhierarchical methods, most popular are “iteration methods” called so because of the redistribution of objects between clusters as a result of several iterations, i.e., repeated application of certain mathematical operations for a gradual approximation to the required result.

Hierarchical methods make it possible to construct dendrogram, which shows that one of the clusters is divided after each clusterization step into two new clusters, while the remaining clusters remain unchanged. If iteration methods are used, the composition of separate clusters can change rather strongly with each clusterization step.

Results obtained by various methods of the cluster analysis can differ appreciably, decreasing the reliability of conclusions made thereby. The reliability will

Table 1. Statistical characteristics of the distribution of contents of chemical elements in FMNC samples from lakes, seas, and oceans

	Fe	Mn	Co	Ni	Cu	Correlation matrix				
Lakes, 102 samples										
Mean, %	18.44	15.02	0.0143	0.0195	0.0559	$r_{cr} = 0.25$	Fe	Mn	Co	Ni
Standard deviation	10.16	11.78	0.0084	0.0196	0.1572	Mn	-0.457			
Variation coefficient, %	55	78	59	101	281	Co	0.209	0.093		
Asymmetry	0.52	0.48	-0.09	1.82	3.18	Ni	0.319	-0.094	0.639	
Excess	-0.39	-1.15	-0.81	3.34	9.18	Cu	0.139	-0.223	0.241	0.213
Seas, 115 samples										
Mean, %	16.45	10.52	0.0122	0.0370	0.0127	$r_{cr} = 0.24$	Fe	Mn	Co	Ni
Standard deviation	8.64	9.64	0.0132	0.0712	0.0295	Mn	-0.478			
Variation coefficient, %	53	92	108	192	233	Co	-0.084	0.372		
Asymmetry	0.06	1.75	2.80	4.55	5.13	Ni	-0.132	0.250	0.572	
Excess	-0.42	3.78	8.92	23.38	31.76	Cu	-0.275	0.126	0.165	0.203
Atlantic Ocean, 284 samples										
Mean, %	19.95	14.03	0.2728	0.2465	0.0972	$r_{cr} = 0.16$	Fe	Mn	Co	Ni
Standard deviation	5.70	6.28	0.1937	0.1808	0.1079	Mn	0.056			
Variation coefficient, %	29	45	71	73	111	Co	0.355	0.462		
Asymmetry	-0.63	0.42	1.56	2.20	3.77	Ni	-0.160	0.657	0.221	
Excess	0.72	0.62	3.87	6.86	20.88	Cu	-0.216	0.264	-0.201	0.386
Indian Ocean, 178 samples										
Mean, %	13.43	15.79	0.2425	0.4474	0.2743	$r_{cr} = 0.19$	Fe	Mn	Co	Ni
Standard deviation	7.18	7.62	0.1671	0.3524	0.3716	Mn	-0.134			
Variation coefficient, %	54	48	69	79	135	Co	0.393	0.207		
Asymmetry	0.87	0.13	1.18	1.46	1.97	Ni	-0.391	0.603	-0.198	
Excess	2.91	-0.34	1.25	1.76	2.97	Cu	-0.362	0.614	-0.306	0.909
Pacific Ocean, 903 samples										
Mean, %	12.81	18.66	0.3234	0.6158	0.3799	$r_{cr} = 0.09$	Fe	Mn	Co	Ni
Standard deviation	5.01	7.35	0.2528	0.3996	0.3321	Mn	-0.270			
Variation coefficient, %	39	39	78	65	87	Co	0.350	0.073		
Asymmetry	0.28	1.05	2.04	1.11	1.53	Ni	-0.426	0.528	-0.141	
Excess	0.99	2.94	5.77	0.73	2.29	Cu	-0.460	0.349	-0.300	0.787

(r_{cr}) Minimum value of the correlation coefficient, with the confidence probability of 99% between contents of chemical elements; significant values of the correlation coefficient are shown in the semibold type.

increase significantly if analogous results are obtained by two independent methods of the cluster analysis.

Among several versions of the hierarchical cluster analysis, we chose Ward's method, because it is more suitable among the hierarchical methods for the analysis of quantitative variables. When applying this method, increment of the sum of squares of the distance from an object to the center of clusters obtained by their combination is accepted as the distance between clusters (Ward, 1963). In contrast to other methods of cluster analysis, the dispersion analysis is applied here to estimate the distance between clusters. At each step of the algorithm, we combine two clusters

that can lead to a minimal increment of the target function, i.e., intragroup sum of squares. This method is designed to combine closely located clusters.

To check the obtained results, the hierarchical Ward's method was supplemented with iterations based on the k -means method described in (Hartigan and Wong, 1979). The k -means algorithm yields k clusters located at the possible greatest distances from each other; i.e., mean contents of chemical elements in various clusters differ maximally from each other.

Calculations were performed with a Statgraphics Plus 2.1 software package. Results of the divisive cluster analysis by Ward's method are presented in Fig. 2.

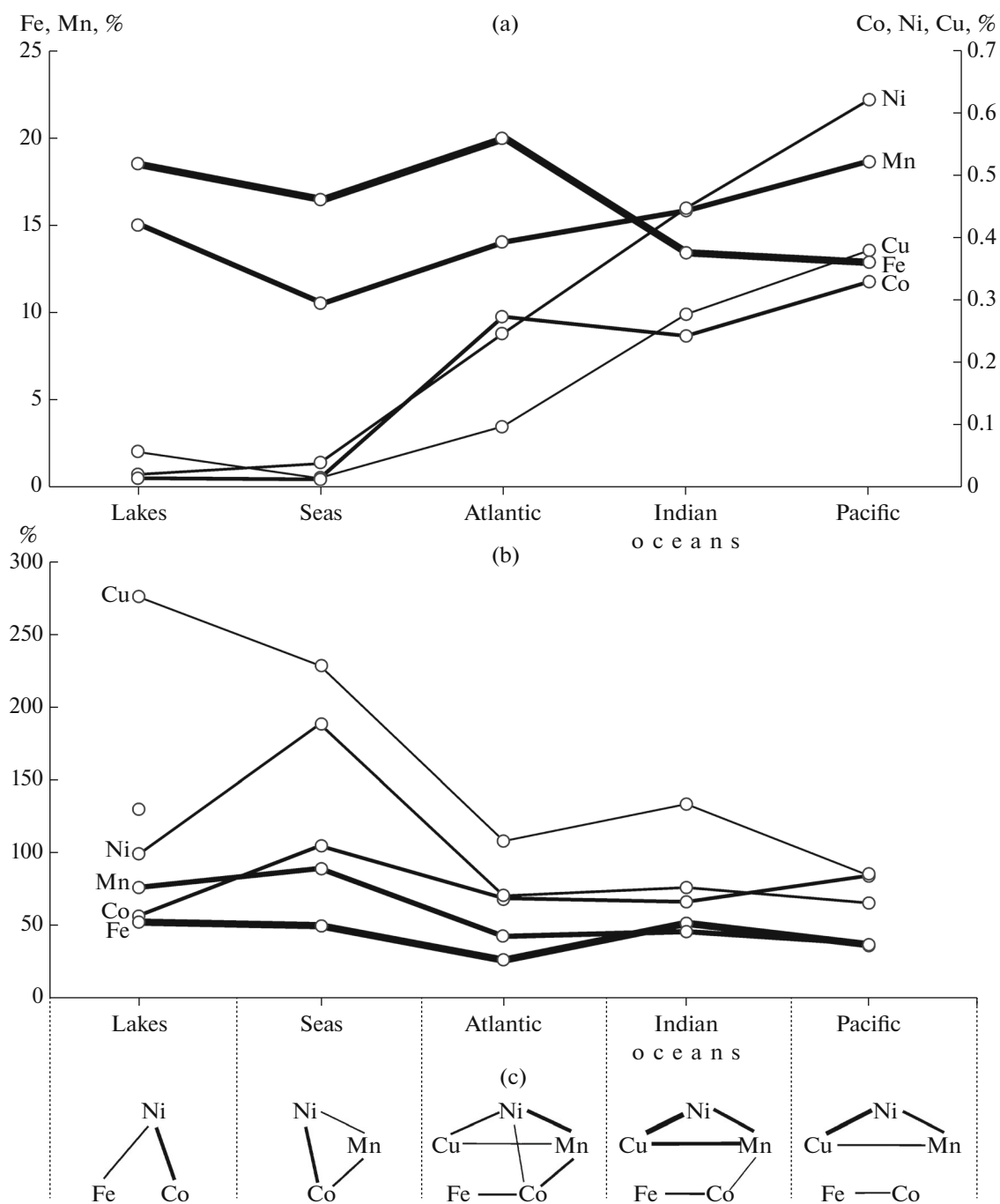


Fig. 1. Mean contents (a), variation of contents (b), and correlation diagrams (c) of chemical elements along the profile: lakes-seas-oceans. Thickness of lines in the correlation diagrams corresponds to the force of correlation links.

The figure shows a hierarchical dendrogram, i.e., successive discrimination of the starting sampling into a growing number of clusters. The number of clusters during this analysis is specified by the researcher. Since it is known beforehand how best to divide the starting sampling into clusters (groups) for the subsequent interpretation, it makes sense to accomplish a stepwise clusterization, i.e., increase the number of clusters by 1 after each step. Clusterization is carried

out until the further discrimination of sampling does not become excessive for the interpretation of results. For the sampling under consideration, clusterization was performed in ten steps; i.e., eleven clusters were obtained at the last step.

To draw the dendrogram, we calculated the mean contents and variation coefficients for each cluster. We also calculated the number of samples representing

lakes, seas, and oceans. The number of FMNC samples taken from various basin types differs markedly (for example, the Pacific samples account for more than one-half of the whole sample population). To judge about the link between a cluster and basin type, we calculated the relative number of samples for each cluster. For example, given that cluster 386 includes 47 samples from lakes and 107 samples from the Pacific Ocean, then these values will correspond to 46% of the total number of lacustrine samples (102) and just 12% of the total number of Pacific samples (903). Hence, the given cluster best characterizes the chemical composition of the lacustrine FMNC. The results of calculations are presented in Table 2 and Fig. 2. In Fig. 2, each cluster corresponds to the box, which includes columnar diagrams demonstrating the relative number (in %) of samples from lakes, seas, and three oceans that make up a specified cluster.

Choice of the number of clusters for the iteration analysis is based on the results of the preceding studies, theoretical considerations, or intuition. One can also perform the sequential analysis of a growing number of clusters and then choose the result providing more possibilities for interpretation. In the present work, we took the results of analysis by Ward's method into consideration and applied the k-means clustering algorithm for the number of clusters ranging from 6 to 11.

RESULTS

Mean contents of Ni, Co, Cu, and Mn in FMNC increase successively in the lakes—seas—oceans profile, and only an elevated Mn content typical of lakes distorts this trend. Mean Fe contents in FMNC decrease in this series. Variation coefficients of the contents of all above-mentioned chemical elements also tend to decrease (Fig. 1, Table 1).

Calculations of the pair correlation functions demonstrate that the number of significant correlations between the considered five chemical elements increases in the lakes—seas—oceans series (i.e., positive correlation with the basin size).

Application of the cluster analysis made it possible to confirm the data on regular variations in the geochemical characteristics of FMNC along the idealized lakes—seas—oceans profile, i.e. in various basin types.

Already step 1 of clusterization of the sampling of FMNC analyses yields a cluster of 230 samples taken from the Pacific and Indian (subordinate) oceans; i.e., the FMNC samples are divided at once based on the basin type.

Only after step 6, however, the obtained seven clusters characterize sufficiently well the series: lakes—seas—Atlantic—Indian—Pacific oceans (Fig. 3, Table 2).

The series begins with clusters 68 and 51 that are marked by the predominance of FMNC samples from lakes, a significant amount of FMNC samples from seas, and the virtual absence of samples from oceans.

The next cluster 386 is composed of the predominant FMNC samples from seas (69%), a significant part of lacustrine samples, and some oceanic samples. At the same time, the oceanic FMNC samples are dominated by the Atlantic and Indian oceans, while the Pacific share is low. Thus, this cluster is dominated clearly by samples from seas, but the share of samples from lakes and oceans is also significant—this fact emphasizes an intermediate position of marine basins between the lacustrine and oceanic basins.

The further series are represented by oceanic clusters: cluster 314 composed of the maximum share of FMNC samples from the Atlantic Ocean and the minimum share from the Pacific; cluster 420 (minimum share of samples from the Atlantic Ocean and maximum share from the Pacific); and cluster 230 (subordinate FMNC samples from the Indian Ocean and predominant samples from the Pacific Ocean). Note that the FMNC formation depth increases gradually from cluster 314 to cluster 230 (Table 3).

Cluster 113 with a small number of the oceanic samples occupies a specific position. It includes Co-rich samples that are almost equally represented in all of the three oceans. Therefore, it is rather difficult to define its position in the profile. S.I. Andreev (1993) distinguished six geochemical types of oceanic nodules and crusts. In terms of contents of the five ore components considered here, one of these types (defined as the cobalt type) is very similar to cluster 113. The cobalt-type nodules and crusts occur in all oceans at a minimum (for the oceanic FMNC) depth of 600–3000 m, while the maximum thickness of the Co-bearing crusts is recorded at a depth of 1200–2200 m (Andreev, 1993).

Calculations of the average depth of FMNC formation in cluster 113 (Pacific Ocean) yielded 2330 m, which is notably lesser than the average depth of FMNC formation in the remaining oceanic cluster population (Table 3). Thus, very high Co contents are related to a relatively small depth of crust formation, i.e., peculiarities of its formation mechanism, probably, typical of all oceans. Specific position of this cluster is also emphasized by its rapid discrimination (already after clusterization step 3).

Further increase of the number (more than seven) of clusters (Fig. 2) only specifies and complicates the obtained result. Cluster 113 is discriminated at step 7. The obtained clusters 21 and 92 differ markedly in terms of the Co content and FMNC formation depth. In cluster 21, the Co content in FMNC is more than two times higher, but the formation depth is almost two times lesser than in cluster 92, once more emphasizing correlation between the Co content and the formation depth of Co-rich FMNC.

Clusterization step 8 leads to the discrimination of cluster 386. Cluster 252 differs weakly from cluster 386, but cluster 134 is characterized by extremely low contents of Fe and Mn. All basin types are represented

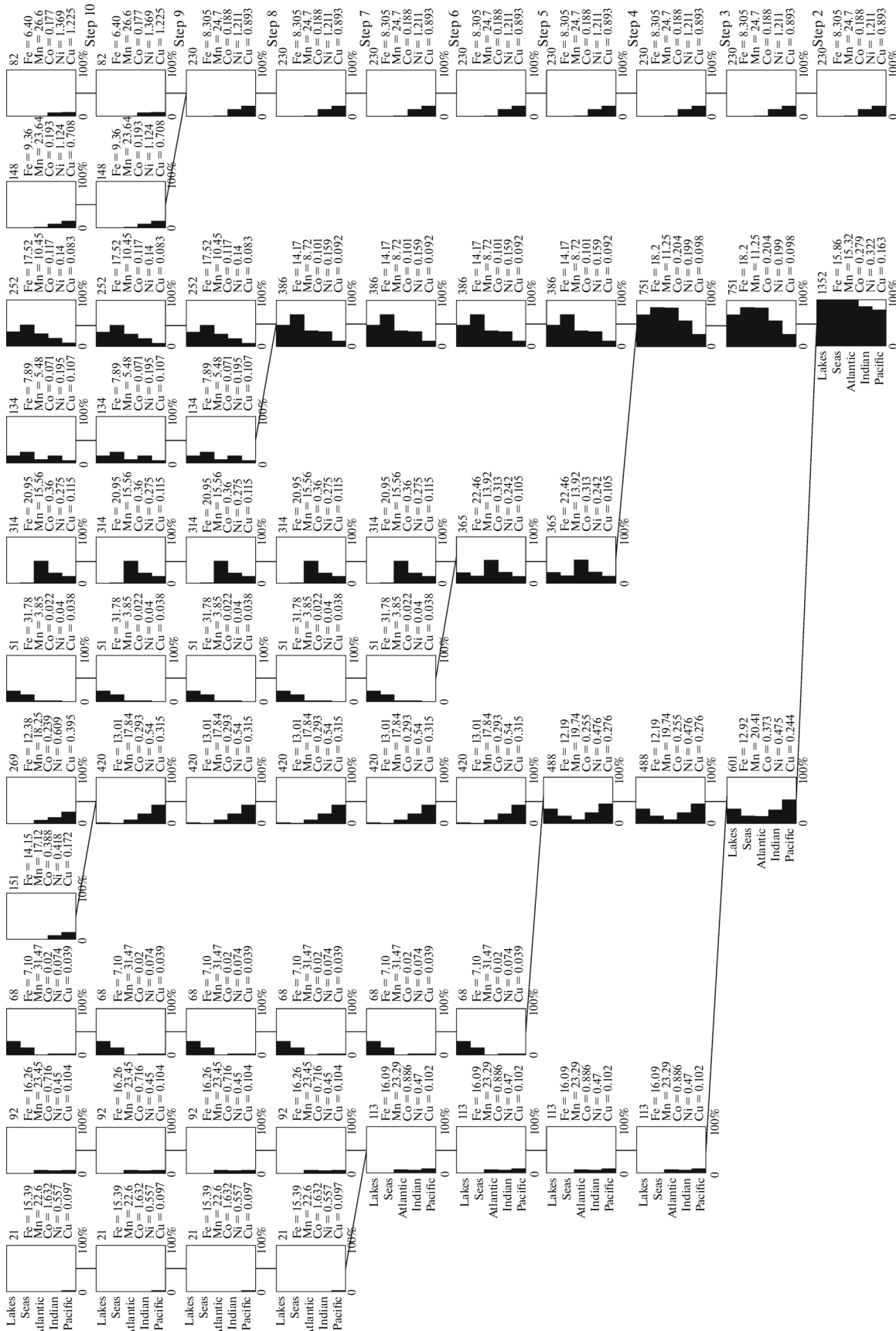


Fig. 2. Dendrogram of the cluster analysis by Ward's method. Each cluster outlined after ten clusterization steps corresponds to the box with bar charts demonstrating the relative number (in %) of samples from lakes, seas, and three oceans that make up a specified cluster. The relative number is calculated as a ratio of the number of samples in the cluster from any basin type to the total number of samples from this basin type. Number on the right side of a box corresponds to the number of samples inside the cluster and simultaneously represents the cluster number. Values given below the cluster number show the mean contents of chemical elements in this cluster. Parental and daughter clusters are tied by lines.

Table 2. Characteristics of clusters calculated by Ward's method

Cluster no.*	Number of FMNC samples, pieces				Relative number of FMNC samples**, %			Mean contents of chemical elements, %				Variation coefficients of chemical element contents, %								
	lakes	seas	oceans		lakes	seas	oceans		Fe	Mn	Co	Ni	Cu	Fe	Mn	Co	Ni	Cu		
			Atlantic	Indian			Pacific	Atlantic											Indian	Pacific
1352	102	115	281	150	704	100	100	99	85	78	15.86	15.32	0.279	0.322	0.163	42	50	99	74	98
230	0	0	3	28	199	0	0	1	15	22	8.31	24.70	0.188	1.211	0.893	32	25	53	27	35
751	70	97	239	100	245	69	85	84	56	27	18.20	11.25	0.204	0.199	0.098	39	49	85	76	98
601	32	18	42	50	459	31	16	15	29	51	12.92	20.41	0.373	0.475	0.244	35	34	92	50	76
488	32	18	22	40	376	31	16	8	23	42	12.19	19.74	0.255	0.476	0.276	35	33	64	52	68
113	0	0	20	10	83	0	0	7	6	9	16.09	23.29	0.886	0.470	0.102	28	34	50	38	78
365	23	18	143	43	138	23	16	50	24	15	22.46	13.92	0.313	0.242	0.105	24	37	54	53	72
386	47	79	96	57	107	46	69	34	32	12	14.17	8.72	0.101	0.159	0.092	43	52	97	100	122
420	2	1	22	37	358	2	1	8	21	40	13.01	17.84	0.293	0.540	0.315	24	19	48	37	54
68	30	17	0	3	18	29	15	0	2	2	7.10	31.47	0.020	0.074	0.039	92	27	91	136	168
314	0	1	137	40	136	0	1	48	22	15	20.95	15.56	0.360	0.275	0.115	17	20	36	38	62
51	23	17	6	3	2	23	15	2	2	0	31.78	3.85	0.022	0.040	0.038	17	82	126	133	168
92	0	0	19	10	63	0	0	7	6	7	16.26	23.45	0.716	0.450	0.104	28	33	31	39	83
21	0	0	1	0	20	0	0	0	0	2	15.39	22.60	1.632	0.557	0.097	24	39	24	29	41
252	32	53	77	30	60	31	46	27	17	7	17.52	10.45	0.117	0.140	0.083	23	36	85	80	102
134	15	26	19	27	47	15	23	7	15	5	7.89	5.48	0.071	0.195	0.107	46	73	122	112	137
148	0	0	3	15	130	0	0	1	8	14	9.36	23.64	0.193	1.124	0.708	25	28	56	29	23
82	0	0	0	13	69	0	0	0	7	8	6.40	26.60	0.177	1.369	1.225	33	18	45	21	19
269	2	1	20	23	223	2	1	7	13	25	12.38	18.25	0.239	0.609	0.395	26	20	56	32	39
151	0	0	2	14	135	0	0	1	8	15	14.15	17.12	0.388	0.418	0.172	16	15	25	34	48

(*) Cluster number corresponds to the number of samples therein. (**) The relative number of FMNC samples was calculated as a ratio of the number of samples in a cluster from any basin type to the total number of samples from this basin type.

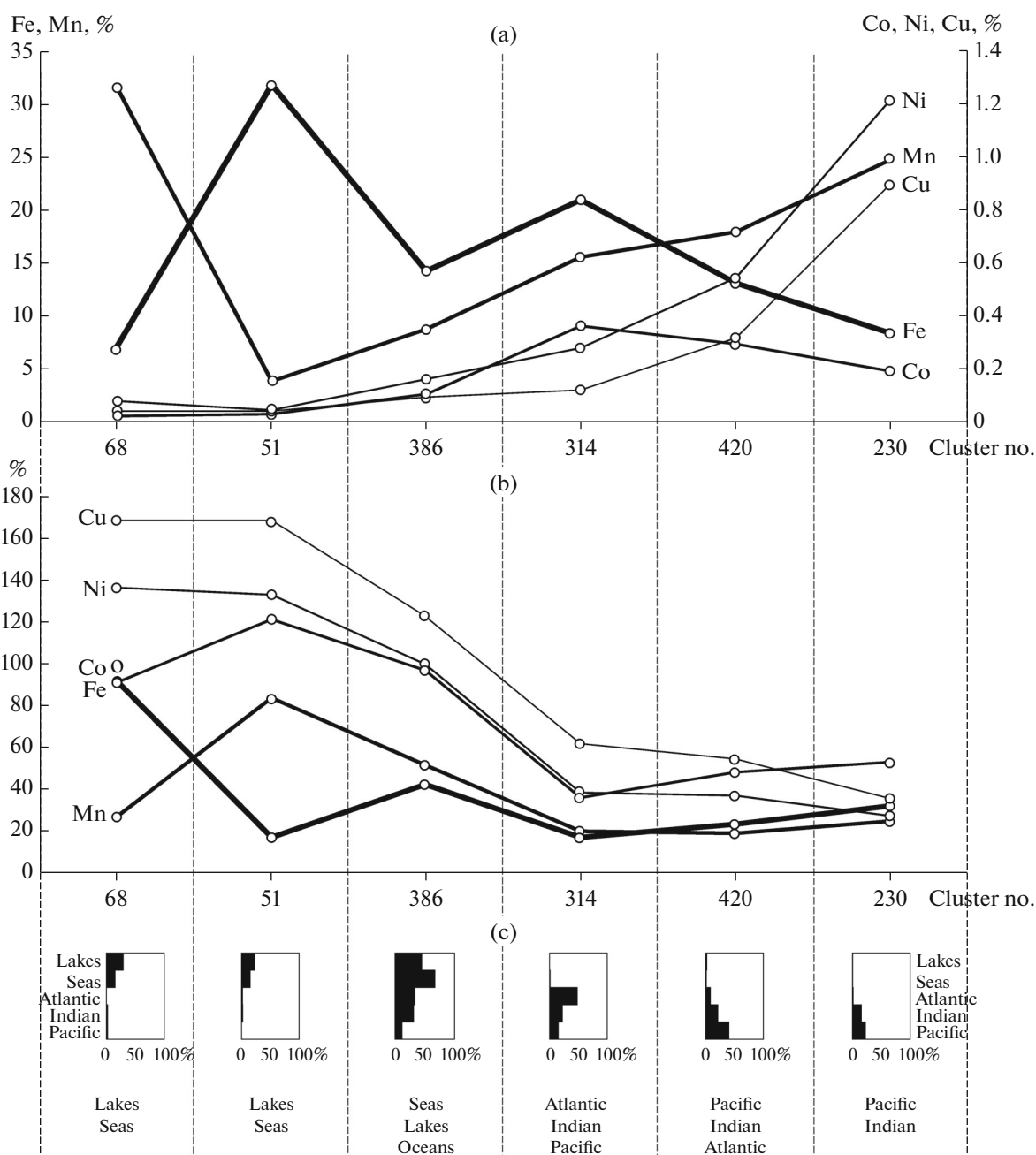


Fig. 3. Distribution of clusters obtained by Ward's method along the profile: lakes-seas-oceans. (a) Distribution of the mean contents of chemical elements in clusters along the profile; (b) distribution of the variation coefficient of chemical element contents in clusters along the profile; (c) bar charts demonstrating the relative number (in %) of samples from lakes, seas, and three oceans that make up a specified cluster.

more or less similarly in this cluster and one gets the impression that it is composed of FMNC samples containing a significant admixture of nonmetallic material that dilutes the ore concentration.

At clusterization step 9, cluster 230 is divided into clusters 82 and 148 that differ weakly from the parental cluster with respect to the contents of Fe, Mn, Co, Ni, and Cu. A similar pattern is also observed at clusterization step 10, where cluster 420 is divided into clusters 151 and 269. Both Pacific cases are marked by the

following feature: among the newly discriminated clusters (82 and 269), the deeper clusters are marked by higher contents of Mn, Cu, and Ni relative to the parental clusters, while contents of Fe and Co are lower. Probably, discrimination of these clusters reflects discrepancies in their formation settings or in sources of ore elements.

As noted above, reliability of the obtained result increases appreciably if a similar result is obtained by two independent methods of the cluster analysis.

Table 3. Average depth of FMNC formation in clusters in the Pacific Ocean

Cluster no.	68	386	314	113	420	230	269	151	82	148
Number of samples	16	98	130	57	338	182	223	135	69	130
Average depth of FMNC formation, m	2840	4230	4040	2330	4450	4690	4700	3950	4850	4610

Application of the *k*-means method as a control procedure revealed the following point: in terms of the characteristic properties, such as the number of samples in cluster, mean contents and variation coefficients of the contents of chemical elements, and the relative number of samples from basins of different types (Fig. 4, Table 4), the obtained results are similar to the data obtained by Ward's method, and the most similar results are obtained when the sampling is divided into nine clusters. Clusters 51, 68, 252, 134, 314, 420, 230, 92, and 21 defined by Ward's method are similar to clusters 64, 79, 238, 159, 365, 337, 186, 127, and 27 obtained with the *k*-means clustering algorithm (Fig. 5). Similarity of the results obtained by two different methods of the cluster analysis makes it possible to predicate validity of the obtained results with a high degree of confidence.

DISCUSSION

Thus, the results obtained by the cluster analysis by Ward's method and confirmed by the *k*-means clustering method revealed the following facts: (a) the results are grouped into clusters in accordance with the FMNC-hosting basin type; (b) concentration of Fe, Mn, Co, Ni, and Cu is influenced significantly by the depth of FMNC formation in oceanic basins.

It is not difficult to see that plots of the mean contents and variation coefficients compiled for the clusters (Figs. 3a, 3b) are generally similar to those presented in Figs. 1a and 1b. Mean contents of the studied elements, except Fe, increase from lakes to oceans, while dispersion of the contents decreases. At the same time, the cluster analysis revealed some specific features that are hidden during usual computations of the mean values, for example, discrimination of the lacustrine samples into three clusters (with strongly different contents of Fe and Mn) and correlation of metal contents with the FMNC formation depth in oceans.

The chemical composition of FMNC depends on the lithofacies and physicochemical settings, formation mechanisms, sedimentation and FMNC growth rates, and contents of the major nodule- and crust-forming components in the near-bottom and interstitial waters.

In FMNC samples from lakes and seas, contents of Ni, Co, and Cu are minimal, but variation coefficients are maximal. Contents of Mn and Fe in the clusters, which characterize FMNC in lakes and seas, are very

different. Their dispersion also demonstrates a contrast variation. For example, the Mn/Fe ratio is 4.4 in cluster 68, 0.1 in cluster 51, and 0.6 in cluster 386. According to (Semenovich, 1973), variations in the Mn/Fe ratio in ferromanganese nodules can be provoked even by minor fluctuations of Eh and pH in the environment. During the microbiological formation of nodules in lakes, Mn is precipitated with the participation of ferrobacteria (they can actively extract both Fe and Mn) and more specialized Mn-depositing microorganisms that are developed in an environment completely suppressed for Fe migration (Zavarzin, 1972). Predominance of a certain type of microorganism in the community can also provoke changes of the Mn/Fe ratio in nodules.

The FMNC formation in lakes and seas is likely related mainly to the diagenetic or biodiagenetic processes (Chukhrov et al., 1989). The FMNC growth rate in lakes is maximal and reaches 1.7–1.8 mm/yr (Shcherbov and Strakhovenko, 2004). Nodules grow rapidly, but they become likewise buried rapidly and cease to grow, because the sedimentation rate is commonly high in small lacustrine basins. Process of the FMNC formation, however, continues for some time under the sediment surface as well. For example, in Lake Oneida (New York, United States), the nodules, which comprise materials deposited from the lake water and occur on the sediment surface, are enriched in Mn but the buried nodules are enriched in Fe (Moore, 1981).

Elements, such as Ni, Co, and Cu, are accumulated in FMNC mainly due to the sorption on manganese and iron oxyhydroxides. Contents of Ni, Co, and Cu in the near-bottom and interstitial waters of lakes are relatively low. Therefore, concentrations of Ni, Co, and Cu in FMNC cannot usually reach significant values in the case of their rapid growth and burial. However, contrast formation settings can provoke a high dispersion of their contents.

The chemical composition of FMNC can be influenced significantly by provenances. For example, the Fe content is very high in nodules from cluster 51 (Table 2, Fig. 2), but the Mn content is low. This cluster is marked by the concentration of FMNC samples from Lake Michigan. The recharge area of this lake accommodates the jaspilite (taconite) pluton of the Lake Superior area. Virtually all rocks of the taconite association are enriched in Fe delivered during the weathering of rocks in this area.

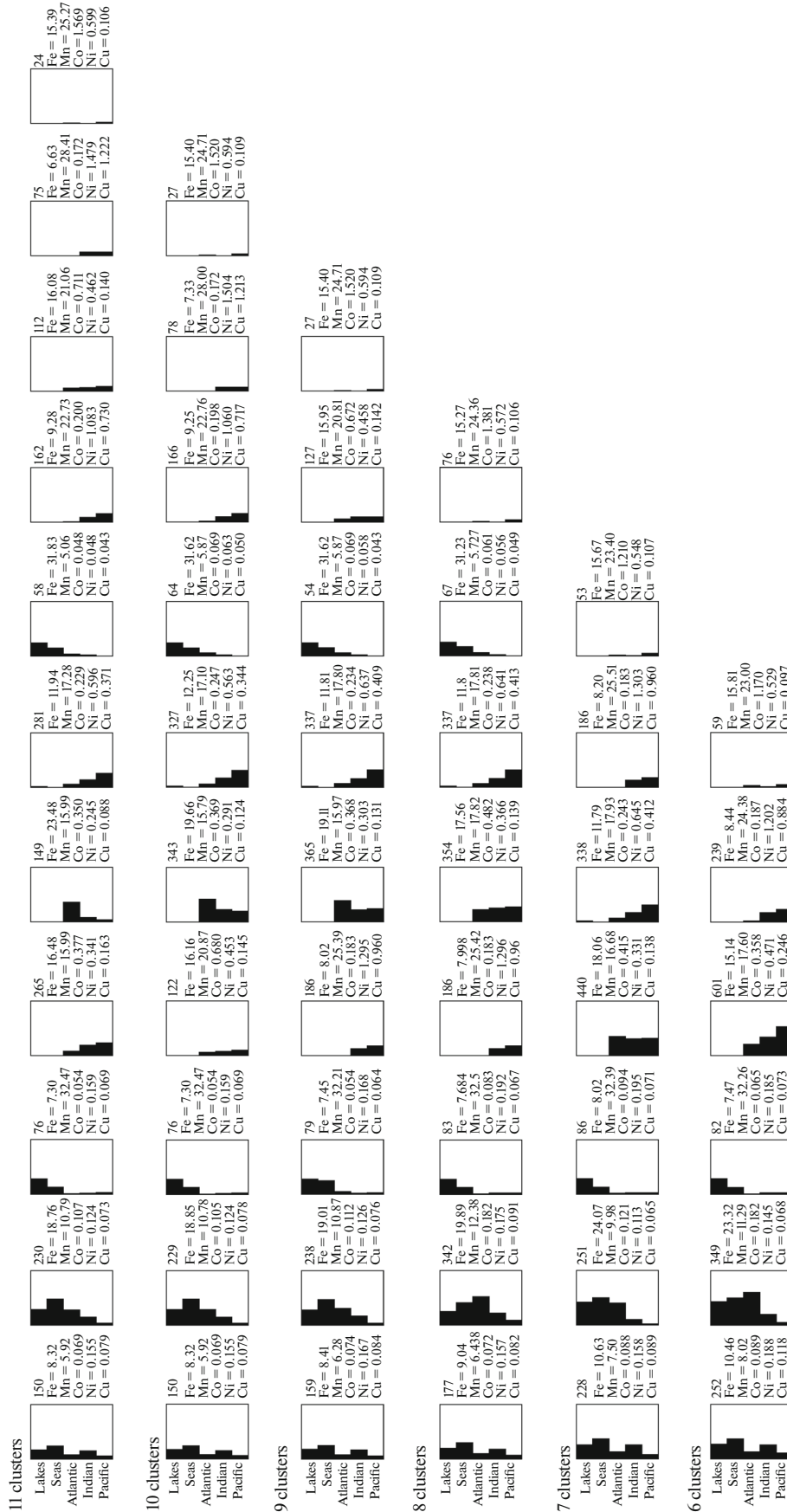


Fig. 4. Results of the k-means cluster analysis obtained for a number of clusters ranging from 6 to 11. See Fig. 2 for explanation.

Table 4. Characteristics of clusters calculated with the k-means clustering algorithm

Cluster no.*	Number of FMNC samples, pieces				Relative number of FMNC samples **, %			Mean contents of chemical elements, %				Variation coefficients of chemical element contents, %							
	lakes	seas	oceans			lakes	seas	oceans		Fe	Mn	Co	Ni	Cu	Fe	Mn	Co	Ni	Cu
			Atlantic	Indian	Pacific			Atlantic	Indian										
6 clusters																			
252	28	43	37	46	98	28	37	13	26	11	10.46	8.02	0.089	0.188	40	59	98	95	116
349	44	57	169	35	44	43	50	60	20	5	23.32	11.29	0.182	0.145	22	43	83	73	96
59	0	0	8	2	49	0	0	3	1	5	15.81	23.00	1.170	0.529	26	36	37	35	61
239	0	0	5	30	204	0	0	2	17	23	8.44	24.38	0.187	1.202	37	24	55	29	36
82	30	15	4	5	28	29	13	1	3	3	7.47	32.26	0.065	0.185	82	23	172	134	152
601	0	0	61	60	480	0	0	21	34	53	15.14	17.60	0.358	0.471	23	21	43	40	64
7 clusters																			
228	27	42	37	46	76	26	37	13	26	8	10.63	7.50	0.088	0.158	41	60	105	98	113
440	0	0	100	55	285	0	0	35	31	32	18.06	16.68	0.415	0.331	19	23	34	36	61
53	0	0	7	1	45	0	0	2	1	5	15.67	23.40	1.210	0.548	25	34	36	34	93
186	0	0	0	23	163	0	0	0	13	18	8.20	25.51	0.183	1.303	48	24	54	28	32
338	2	0	21	31	284	2	0	7	17	31	11.79	17.93	0.243	0.645	26	20	52	31	42
86	30	15	5	5	31	29	13	2	3	3	8.02	32.39	0.094	0.195	78	22	176	127	158
251	43	58	114	17	19	42	50	40	10	2	24.07	9.98	0.121	0.113	23	49	96	89	141
8 clusters																			
177	20	34	29	32	62	20	30	10	18	7	9.04	6.44	0.072	0.157	44	68	112	105	116
342	26	47	149	40	80	25	41	52	22	9	19.89	12.38	0.182	0.175	16	30	66	64	89
36	0	0	2	0	34	0	0	1	0	4	15.27	24.36	1.381	0.572	27	36	31	30	44
186	0	0	0	23	163	0	0	0	13	18	8.00	25.42	0.183	1.296	34	23	54	25	32
354	0	0	63	45	246	0	0	22	25	27	17.56	17.82	0.482	0.366	20	24	31	37	64
337	2	0	21	29	285	2	0	7	16	32	11.80	17.81	0.24	0.64	26	20	50	32	41
67	25	19	16	4	3	25	17	6	2	0	31.23	5.73	0.061	0.056	16	82	146	113	148
83	29	15	4	5	30	28	13	1	3	3	7.68	32.50	0.083	0.192	79	22	167	130	150
9 clusters																			
159	18	29	24	30	58	18	25	8	17	6	8.41	6.28	0.074	0.167	43	68	117	101	113
238	29	54	87	30	38	28	47	31	17	4	19.01	10.87	0.112	0.126	16	38	83	80	106
79	29	15	4	5	26	28	25	5	2	3	7.45	32.21	0.054	0.168	82	22	161	137	148
186	0	0	0	23	163	0	0	0	13	18	8.02	25.39	0.183	1.295	36	22	54	24	32
365	0	0	112	40	213	0	0	39	22	24	19.11	15.97	0.368	0.303	20	21	25	35	58

Table 4. (Contd.)

Cluster no.*	Number of FMNC samples, pieces				Relative number of FMNC samples**, %				Mean contents of chemical elements, %				Variation coefficients of chemical element contents, %								
	lakes	seas	oceans			lakes	seas	oceans			Fe	Mn	Co	Ni	Cu						
			Atlantic	Indian	Pacific			Atlantic	Indian	Pacific											
127	0	0	18	17	92	0	0	6	10	10	15.95	20.81	0.672	0.458	0.142	23	29	23	34	93	
64	24	17	16	4	3	24	15	6	2	0	31.62	5.87	0.069	0.058	0.043	15	81	146	116	145	
337	2	0	21	29	285	2	0	7	16	32	11.81	17.80	0.234	0.637	0.409	26	20	46	32	41	
27	0	0	2	0	25	0	0	1	0	3	15.40	24.71	1.520	0.594	0.109	24	39	27	31	46	
10 clusters																					
150	17	28	24	27	54	17	24	8	15	6	8.32	5.92	0.071	0.155	0.082	44	70	122	104	120	
229	30	55	81	27	36	29	48	29	15	4	18.85	10.78	0.105	0.124	0.078	16	38	85	84	124	
76	29	15	3	4	25	28	13	1	2	3	7.44	32.47	0.057	0.156	0.063	83	22	183	145	168	
122	0	0	18	15	89	0	0	6	8	10	16.16	20.87	0.680	0.453	0.145	22	29	22	34	100	
343	0	0	118	41	184	0	0	42	23	20	19.66	15.79	0.369	0.291	0.124	18	21	25	36	57	
327	2	0	17	30	278	2	0	6	17	31	12.25	17.10	0.248	0.563	0.344	23	19	44	31	43	
64	24	17	16	4	3	24	15	6	2	0	31.62	5.87	0.069	0.063	0.050	15	81	146	148	193	
166	0	0	5	17	144	0	0	2	10	16	9.25	22.76	0.198	1.060	0.717	32	18	59	24	25	
27	0	0	2	0	25	0	0	1	0	3	15.40	24.71	1.520	0.594	0.109	24	39	27	31	46	
78	0	0	0	13	65	0	0	0	7	7	7.33	28.00	0.172	1.504	1.213	72	27	45	28	23	
11 clusters																					
150	17	28	24	27	54	17	24	8	15	6	8.32	5.92	0.069	0.155	0.079	44	70	118	104	114	
230	30	55	80	27	38	29	48	28	15	4	18.76	10.79	0.107	0.124	0.073	15	38	86	82	110	
112	0	0	17	13	82	0	0	6	7	9	16.08	21.06	0.711	0.462	0.140	22	30	22	34	101	
265	0	0	24	34	207	0	0	8	19	23	16.48	15.99	0.377	0.341	0.163	14	19	25	31	48	
149	0	0	101	15	33	0	0	36	8	4	23.48	15.99	0.350	0.245	0.088	12	24	30	39	64	
281	2	0	18	25	236	2	0	6	14	26	11.94	17.28	0.229	0.596	0.371	25	20	45	28	40	
58	24	17	11	4	2	24	15	4	2	0	31.83	5.06	0.048	0.048	0.043	16	82	158	120	154	
76	29	15	3	4	25	28	13	1	2	3	7.30	32.47	0.054	0.159	0.069	85	22	188	144	171	
24	0	0	2	0	22	0	0	1	0	2	15.39	25.27	1.569	0.599	0.106	24	39	26	33	46	
75	0	0	0	13	62	0	0	0	7	7	6.63	28.41	0.172	1.479	1.222	40	22	46	22	23	
162	0	0	4	16	142	0	0	1	9	16	9.28	22.73	0.200	1.083	0.730	31	19	58	24	25	

(*) Cluster number corresponds to the number of samples therein. (**) Relative number of FMNC samples was calculated as a ratio of the number of samples in the cluster from any basin type to the total number of samples from this basin type. Calculations with the k-means clustering algorithm were accomplished for the number of clusters ranging from 6 to 11.

Heterogeneity of the chemical composition of FMNC samples from lakes and seas due to their extremely diverse physicochemical and lithofacies settings in different basins (sometimes, within a single basin) leads to high variation coefficients of the contents and attenuation of correlations between elements, i.e., decrease of the number of significant correlations. In the cluster analysis, this heterogeneity is emphasized by the discrimination of samples into three clusters with highly different contents of Fe and Mn in FMNC. At the same time, contents of Ni, Co, and Cu in them are low, but they are characterized by high dispersion.

The presented calculations show that contents of Mn, Ni, Cu, and Co are maximal in oceans, but their variation coefficients are minimal. Contents of chemical elements in FMNC depend on the mineral composition, lithofacies settings of nodule formation, ocean depth, sedimentation and FMNC growth rates, bioproductivity of the water column, hydrodynamic settings, and so on.

The FMNC formation rate is one of the significant parameters. For example, the FMNC growth rate is high (as much as 1.7–1.8 mm/yr) in lakes, but slightly lower in the seas and oceanic periphery. The rate of ferromanganese crust overgrowth on the drill string recovered from a depth of 200 m near the Californian coast was 1 mm/yr (Mereau, 1969), but the oceanic FMNC growth rate does not usually exceed 5 mm/Ma and can reach more than 40 mm/Ma in rare cases.

It should, however, be noted that FMNC can likely grow irregularly and, probably, with prolonged pauses. For example, according to (Barnes and Dymond, 1967), the FMNC growth continued for just 10% of their residence time on the sediment surface. As is known, Ni, Cu, and Co are absorbed and deposited simultaneously with oxyhydroxides. Moreover, according to (Savenko, 2004), the oxyhydroxides are responsible for 80–100% of the contents of these elements in nodules. So, if we take into consideration these facts, it becomes evident that possibilities of the sorption of Ni, Cu, and Co on the oxyhydroxide substrate increase significantly in the case of a prolonged residence of FMNC on the sediment surface.

An important role in the accumulation of ore components in FMNC is played by their formation depth, which significantly governs the sedimentation rate. Such formations are marked by the maximal (in terms of area and ore component contents) development in the deep-water parts of oceans. They are confined to pelagic sediments characterized by the minimal sedimentation rates (1–3 mm/ka) and to seamounts that are also characterized by low sedimentation rates. This is not surprising, because the higher the sedimentation rate, the more rapidly such nodules and crusts are buried under the sediment and the lesser possibilities for the formation of ore concentrations.

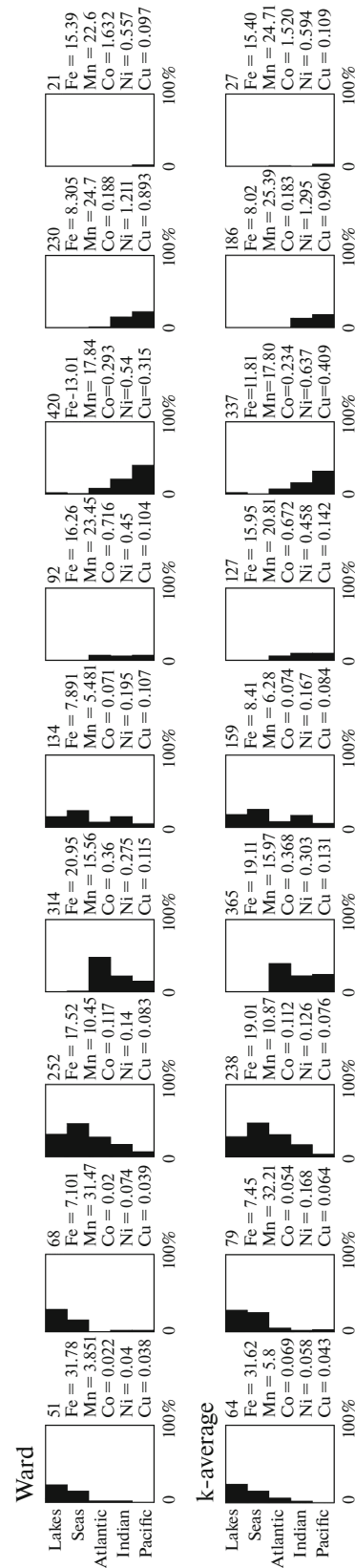


Fig. 5. Comparison of clusters obtained by Ward's method (a) and k-means method (b). See Fig. 2 for explanation.

Table 5. Input of Mn and Fe into the World Ocean, according to (Savenko, 2004)

Source	Total material flow, Gt/yr	Concentration, ppm		Input, Mt/yr	
		Mn	Fe	Mn	Fe
	Dissolved forms				
River runoff	40 300	0.008	0.040	0.32	1.64
Underground runoff	2400	0.049	0.547	0.12	1.31
Submarine hydrothermal solutions	55*	44	100	2.42	5.50
	Suspended forms				
River runoff	18.5	1100	51 000	20.35	943.5
Coastal abrasion	0.5	1160	50 400	0.58	25.18
Ice rafting	1.5	1160	50 400	1.74	75.54
Eolian transport-	0.87*	850	38 000	0.74	33.06

(*) Data from (Savenko, 2004). Other total flows of material: suspended river runoff, coastal abrasion, and ice-rafting (Lisitzyn, 1974); river runoff (Gordeev, 1984); underground runoff (Zektser et al., 1984). Concentrations of chemical elements: river runoff of the dissolved material (Gordeev, 1984); submarine hydrothermal solutions (Thompson, 1983); underground runoff of the dissolved material in the active water exchange zone (Shvartsev, 1998). The content of chemical elements in the solid material transported to ocean by glaciers and coastal abrasion is accepted to be equal to that in the Earth's crust and soils, respectively, for rocks and eolian material (Gordeev, 1984).

Some chemical elements demonstrate an explicit link with the FMNC formation depth. For example, nodules and crusts in the Pacific Ocean display increase of the Cu content and decrease of Co with increasing depth (Skorniyakova, 1976). Our data confirm this trend: cluster 230, which is characterized by maximal depths of FMNC formation, includes nodules with the maximal (for the oceanic clusters) contents of Cu and minimal contents of Co; the nodules and crusts recovered from the shallowest-water cluster 113 are marked by minimum Cu and maximum Co.

Some researchers believe that the FMNC formation depth completely governs their composition and deposition intensity. For example, L.I. Anikeeva et al. (2005) define four different-depth hydrochemical zones, each characterized by specific proportions of the major ore components in FMNC. Thus, the genetic and ore-geochemical diversity of products of the ferromanganese ore genesis in the oceanic water mass is governed mainly by the vertical geochemical zonation.

The source of ore material is also important for the FMNC formation. In lakes and marginal seas, the FMNC material is derived mainly from land. In oceans, however, sources of Fe, Mn, Cu, Ni, Co are polygenous. These elements are related to the riverine and groundwater discharges, submarine hydrothermal activity, eolian transport, and glacial drift.

Table 5 shows estimates of the budget of Mn and Fe input into the World Ocean according to (Savenko, 2004). A major portion of the dissolved Fe and Mn is contributed by the submarine hydrothermal solutions. Volumes of their input with the suspended matter (particulates) are two times higher relative to the dissolved form. However, more than 90% of the particulates do not reach the open ocean and is deposited at

the river–sea barrier, in aprons, or along the oceanic periphery. The amount of particulates succeeding to reach the pelagic zone is estimated at about 7% (Savenko, 2004) or 7.8% (Gordeev, 2009).

The river runoff is accomplished in the suspended and dissolved forms. Moreover, the mass of suspended matter is many times higher than that of the dissolved material. The discharge of solid materials is estimated at 18.6 Gt/yr and the total discharge of dissolved material in ocean is 4636 Mt/yr, including 17.8 Mt of trace elements (Gordeev, 2009). However, only a negligible portion of the river runoff reaches the oceanic depths. The major portion (up to 95% of the solid discharge and a significant part of the dissolved material) remains in the river–sea barrier zone, but values of the pure discharge are none the less sufficiently high (Gordeev, 2009) (Table 6). These significant masses of the river discharge, which are represented by the finest fractions of the suspended matter (i.e., particulates), surmount the river–sea barrier and scatter over the basin according to laws of the mechanical differentiation.

As compared to the coarser fractions, the particulates are always enriched in Co, Ni, Cu, Mo, Pb, Zn, and other trace elements. Moreover, the finer the suspended matter, the higher is the concentration of element. The finest (subcolloidal and colloidal) particulates with the highest concentrations of these elements are transported to the most distal zones of the basin during the mechanical migration of the riverine suspended matter. Hence, pelagic sediments are more enriched in Cu, Mn, Co, Ni, and other elements than the coastal (coarser) sediments. According to (Strakhov, 1968), the finest fraction is delivered to the pelagic zone and distinctly enriched in the above-listed elements in the case of long-term transport to basins with large water areas; therefore, contents of Mn, Ni, Co, Cu, Mo, Pb, and Zn increase gradually

Table 6. Volumes of chemical elements delivered to the oceanic water by the high-temperature hydrothermal solutions and river runoffs, according to (Bogdanov et al., 2015)

Element	Content in the hydrothermal solution, g/kg	Number of determinations	Hydrothermal flows (H), g/yr	Pure river runoff, t/yr (Gordeev, 2009)		Ratio of flows	
				solution (S)	total (solution + particulates) (T)	H/S	H/T
Fe	0.246	37	2.75×10^7	1.4×10^6	9.6×10^7	20	0.3
Mn	0.0714	36	7.8×10^6	3.2×10^5	8.5×10^6	25	0.9
Cu	0.00154	27	1.6×10^5	5.8×10^4	0.2×10^6	2.8	0.8
Co	0.0000245	11	2.75×10^3	3.0×10^3	3.8×10^4	0.92	0.072

in the pelagic sediments; when concentrations of elements exceed the Clarke level, they make up the embryonal-ore concentrations; further, the accumulative process continues during diagenesis; and finally, embryonal-ore accumulations are converted into real ore deposits.

However, it has become evident now that this mechanism can only be applied partly to processes of the oceanic sedimentation and FMNC formation. Biota plays a significant role in the oceanic lithogenesis. In addition to the mechanical differentiation, the biological differentiation of material is very important in ocean. Precisely owing to a wide development of processes related to such differentiation (bioassimilation, biofiltration, biosorption, and biotransport), which foster biotransformation of the dissolved and suspended forms of elements, and owing to high intensity of water mixing in the World Ocean, the genetic signature of Fe, Mn, Cu, Ni, and Co becomes fuzzy in oceans, hampering identification of the sources of these elements in FMNC. That is why the most productive FMNC fields are spatially unrelated to zones with hydrothermal activity, although the hydrothermal influx is among major sources of the dissolved Mn in oceans. It is also sufficiently obvious that not only diagenetic processes are responsible for the FMNC formation. Convincing arguments have been proposed in numerous publications in favor of the hydrogenic, sedimentary-diagenetic, biogenic-diagenetic, and halmyrolitic mechanisms of FMNC formation. According to recent concepts, oxide ores can be considered a fundamentally new form of ferromanganese stromatolites. Differences in the formation mechanism lead to variations in the proportions of metals in FMNC. These distinctions are not always easily discernible. Therefore, the cluster analysis has a great perspective for the discrimination of geochemically similar FMNC samples, given that a sufficiently large geochemical database is available.

Serious problems arise when we attempt to calculate the amount of Fe, Mn, and other elements delivered by hydrothermal solutions to the ocean. Researchers tried many times to estimate the flow of hydrothermal solutions from the oceanic crust to the near-bottom water. According to (Bogdanov and

Lein, 2010), the results reported so far differ by several orders of magnitude, but the most representative results were obtained by M. Palmer and J. Edmond who estimated the rate of hydrothermal solution flow into ocean at $1.1 \pm 0.2 \times 10^{14}$ kg/yr. According to (Savenko, 2004), the flow rate is $0.55 \pm 0.15 \times 10^{14}$ kg/yr.

Since the composition of hydrothermal solutions is extremely variable (Bogdanov and Lein, 2010) and the number of its determinations is relatively small, estimates of the average values of flows for individual elements can significantly differ both from one another and from the real average values. For example, the hydrothermal flow of Mn is estimated at 7.8 Mt/yr in (Bogdanov and Lein, 2010) but no more than 0.5 Mt/yr in (Volkov, 1993). All these facts force us to take the representativity of such estimates with great care.

Application of the cluster analysis unraveled two groups of elements in terms of their behavior in oceans: (i) Fe and Co; (ii) Mn, Cu, and Ni. Contents of Mn, Cu, and Ni in FMNC increase from the relatively shallow-water cluster 314 dominated by the Atlantic samples to the deep-water clusters 420 and 230 dominated by the Pacific samples. An opposite correlation is typical of Fe and Co. Table 6 shows the data adopted from (Bogdanov et al., 2015). These data show that Fe and Co differ appreciably from Mn and Cu with respect to the proportion of hydrothermal and riverine flows. As is known, the share of volcanic material in sediments of the Pacific Ocean is highest relative to other oceans. Probably therefore, the Pacific nodules and crusts are marked by higher values of the average concentration of Mn, Cu, and Ni, which are delivered actively by hydrothermal solutions but slightly depleted in Fe and Co, which are delivered mainly by the river runoff. The decrease of Fe can also be related to its lower (relative to Mn) migration capacity in the reducing or weakly reducing environment, promoting a selective concentration Mn and appreciable increase of the Mn/Fe ratio (Savenko, 2004).

CONCLUSIONS

1. Statistical processing of more than 1500 chemical analyses of FMNC revealed that contents of Fe, Mn, Cu, Ni, and Co vary regularly in the idealized

profile: lakes—seas—oceans. Data obtained for the mean contents, variation coefficients, and correlation coefficients are similar to the results of cluster analysis, testifying to a real existence of these regularities that can be identified more clearly based on the discrimination of samples into clusters.

2. Discrimination of FMNC samples from lakes and seas into three clusters with contrast Fe and Mn contents reflects a significant variability of the physicochemical and lithofacies settings of FMNC formation. This fact is also suggested by the high dispersion of metal contents and their weak intercorrelations.

3. High concentrations of Mn, Cu, Co, and Ni in the oceanic FMNC reflect the combined influence of several processes: first, the input of a significant volume of metals with the hydrothermal flow (primarily, in the Pacific Ocean); second, the enrichment of pelagic zones of oceanic basins with the most mobile elements due to the mechanical fractionation of particulates; and third, the large-scale biological differentiation in oceans. The decrease of Fe in FMNC in the lakes—seas—oceans profile is provoked by its lower (relative to Mn) migration capacity, leading to the selective concentration of Mn. Application of the cluster analysis made it possible to decipher regular variations in Mn, Cu, Co, and Ni concentrations depending on the FMNC formation depth.

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