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OCEANOLOGY

Germanium-Rich Crusts of the Sea of Japan

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Abstract—Ore crusts with a germanium content of up to 96 ppm were discovered in the Sea of Japan. This is tens of times higher than the clarke of the Earth's crust. Germanium-rich crusts were dredged together with intermediate and felsic volcanic rocks. The crusts are composed predominantly of iron oxyhydroxides (goethite) and contain germanium in the dispersed state.

Keywords: germanium, ferromanganese crusts and concretions, Sea of Japan

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INTRODUCTION

To support the technological sovereignty of this country, the Russian Academy of Sciences together with other institutions has been instructed to determine the priorities for the long-term development of the mineral resource base of solid commercial minerals. Germanium is included in the list of the main types of strategic mineral resources and, therefore, is in the sphere of priority attention [1]. Currently, the main sources of germanium are considered to be stratiform polymetallic and lignite deposits (germanium content in sphalerite exceeds 100 g/t, in coal—200 g/t) [2, 3].

Ferromanganese concretions and crusts (ferromanganese formations, FMFs) on the bottom of oceans and seas are classified as solid commercial minerals and are promising for industrial extraction of nickel, copper, cobalt, manganese, and a number of other strategically important metals. Very little is known about the distribution of germanium in FMFs. Few publications report on diagenetic, sedimentary (sedimentary, hydrogenetic), or sedimentary–diagenetic FMFs and testify to a low content of germanium at the level of 1–2 g/t [4–6], which approximately corresponds to the clarke for the upper part of the continental crust. By various estimates, the clarke values range from 1.3 to 1.6 g/t [7]. There are reasons to assume that hydrothermal FMFs are enriched in germanium. The content of this element in post-magmatic high-temperature aqueous fluids and mineral-forming solutions, which formed hydrothermal mineralization of various deposits, averages 17 g/t with a maximum value of 930 g/t [8]. A dispersion halo of germanium in water is a reliable indicator of the discharge of hydrothermal solutions to the seafloor [9].

The purpose of this work is to study the special features of the germanium distribution in FMFs formed with the participation of a hydrothermal source of matter.

MATERIALS AND METHODS

We studied 29 samples of FMFs from the summit parts of volcanic edifices of the Sea of Japan and nine samples of volcanic rocks composing these edifices (Figs. 1, 2; Table 1). The material was dredged during cruises of the R/V *Pervenets i*n 1975–1980 and was partially studied [10–12]. The Sea of Japan is located in the continent–ocean transition zone. The sea is known for intensive volcanic and post-volcanic hydrothermal activity. FMFs, developed on volcanic edifices of the Sea of Japan, are of hydrothermal–sedimentary origin [13] and are associated with volcanic rocks of two formation–geochemical types: post-rift (the absolute majority of FMFs) and marginal–continental [14]. Volcanic rocks of the post-rift type are basically basalts. They compose volcanic edifices in deep-water basins with newly formed Cenozoic (sub)oceanic crust (mantle mafic volcanism). In our study, this type of volcanic rocks is represented by samples from the Galagan, Evlanov, Gebass, and Koltso rises (Fig. 1, Table 1). Volcanic rocks of the marginal–continental type are mainly andesites, dacites, and rhyolites, as well as trachydacites and trachy-

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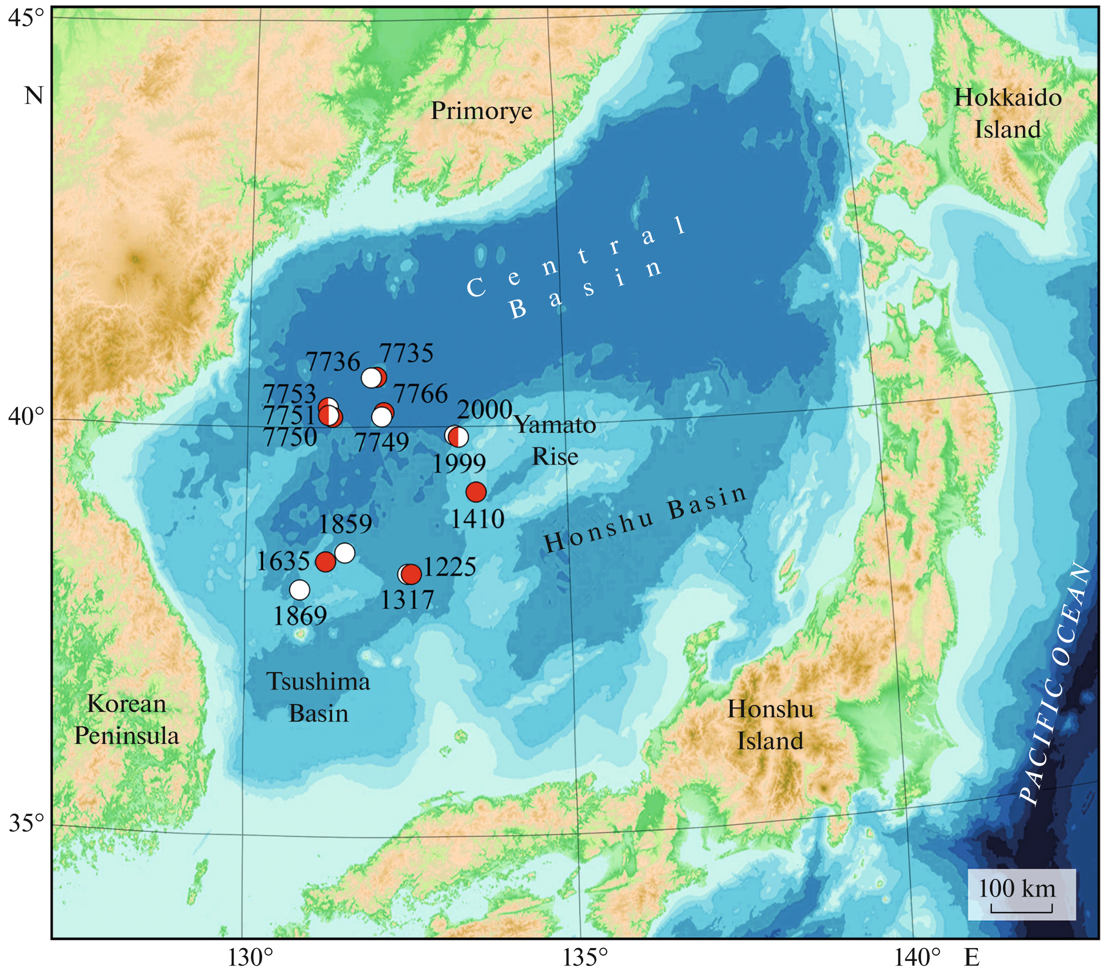

Fig. 1. Map of the Sea of Japan with the largest morphological elements of the bottom and dredging stations of FMFs (red circles) and volcanic rocks (white circles). Stations 1635, 1859, and 1869, Krishtofovich Rise. Stations 1410, 1999, and 2000, North Yamato Ridge. Stations 1225 and 1317, Galagan Rise. Stations 7735 and 7736, Gebass Rise. Stations 7750, 7751, and 7753, Yevlanov Rise. Stations 7749 and 7766, Koltso Mount. The cartographic base was compiled from The General Bathymetric Chart of the Oceans (GEBCO) 2022 data.

rhyolites. They compose the superimposed volcanic edifices within large rises with the Proterozoic–Mesozoic ancient (sub)continental crust (crustal andesite–rhyolite volcanism). In our study, this type of volcanic rocks is represented by samples from the Krishtofovich Rise and the North Yamato Ridge (Fig. 1; Table 1).

Analytical studies were carried out in the Primorskii Center for Local Elemental and Isotopic Analysis, Far East Geological Institute, Far East Branch, Russian Academy of Sciences, Vladivostok. For elemental analysis, samples of FMFs and volcanic rocks were preliminarily abraded, dried at 105–110°C to constant weight, and were affected by open acid decomposition ($HF + HNO_3 + HClO_4$). For FMFs, a sample weight of the suspension was 30 mg, and for volcanic rocks, 50 mg. Loss on ignition and the silica content in samples were determined by gravimetry; other macroelements, by atomic emission spectrometry with inductively coupled plasma on a Thermo iCAP 7600 Duo spectrometer (United State). The content of trace elements, including germanium, was analyzed by inductively coupled plasma mass spectrometry on an Agilent 8800x quadrupole spectrometer (Japan) according to the method proposed previously [15], optimized for germanium. Germanium was determined by the ^{74}Ge isotope. Polyatomic interference from nickel, iron, potassium, and double-charged rare earth elements was eliminated by the background correction using a helium-filled collision cell of the spectrometer. Foreign and domestic standard samples of FMFs and rocks were used for quality control of the chemical element determinations (Table 2). The accuracy of the results of the element determinations was assessed by the values of the relative standard deviation (RSD). For macroelements, the error did not exceed 2–5%; for most trace elements, the RSD was 15–20% or less; for germanium, it was less than 18% (Table 2), which corresponds to the quality criteria for quantitative ele-

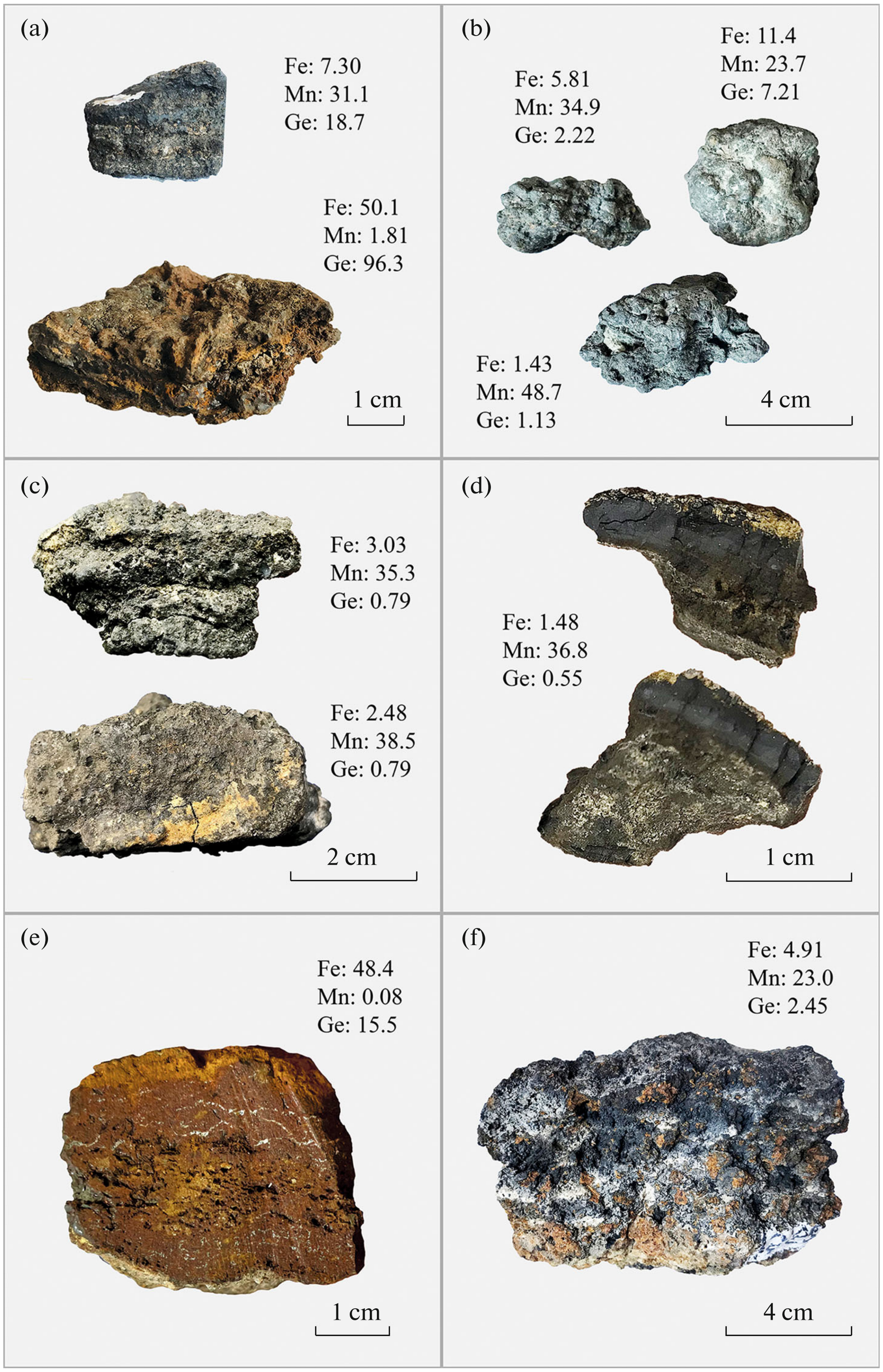

Fig. 2. The general view of FMFs of the Sea of Japan with indication of the average content of iron (wt %), manganese (wt %), and germanium (g/t). (a) Station 1635; (b) station 1999; (c) station 7753; (d) station 7766 (a chip of the sample); (e) station 1410 (a cross-cut of the sample); (f) station 1225. See Fig. 1 for the location of the stations.

mental analysis in geochemical studies [17]. The databases compiled for FMFs and volcanic rocks were processed using multivariate statistics methods (Supplementary Information). During the correlation analysis, the relationships of germanium with other chemical elements were established. Taking into consideration the strongest positive relations in the space of the main factors, geochemical groups were distinguished and the position of germanium was fixed. The germanium-bearing mineral phases were searched in a

Table 1. Iron, manganese, silica, and germanium content in FMFs and volcanic rocks of the Sea of Japan

Station number	Type of material	Samples, *n*	Analyses, *n*	Fe, wt %	Mn, wt %	Si, wt %	Ge, g/t
Krishtofovich Rise							
1635	Ferromanganese and ferruginous crusts and concretions	5	7	(6.63, 50.1) 24.7	(1.81, 31.4) 19.8	(4.4, 9.48) 7.01	(15.9, 96.3) 41.5
1859	Rhyolite	1	1	0.86	0.01	35.0	1.30
1869	Rhyolite	1	1	1.33	0.01	31.7	1.34
North Yamato Ridge							
1410	Ferruginous crusts	10	10	(46.0, 54.4) 50.3	(0.06, 0.15) 0.09	(2.52, 9.13) 5.71	(15.0, 17.1) 16.0
1999	Ferromanganese and manganese crusts and concretions	3	7	(0.68, 16.2) 6.97	(11.3, 50.7) 34.0	(1.74, 18.2) 8.64	(0.97, 7.85) 4.05
	Andesite	1	1	5.59	0.10	25.1	1.07
2000	Andesite	1	1	4.86	0.09	27.1	1.04
Evlanov Rise							
7750	Ferromanganese crust	1	2	(13.1, 17.5) 15.3	(1.76, 13.9) 7.83	(21.4, 27.0) 24.2	(8.31, 10.4) 9.38
7751	Ferromanganese crust	1	1	12.6	19.5	15.5	1.41
	Basalt	1	1	5.91	0.06	22.5	1.11
7753	Essentially manganese crusts	4	8	(0.14, 7.09) 2.21	(28.0, 43.8) 38.0	(0.51, 12.0) 4.70	(0.55, 1.25) 0.82
	Basalt	1	1	7.82	0.08	21.8	1.12
Galagan Rise							
1225	Ferromanganese crust	1	3	(1.64, 9.02) 4.91	(7.65, 35.5) 23.0	(4.42, 16.9) 10.2	(2.33, 2.58) 2.45
1317	Basalt	1	1	6.88	0.06	21.8	1.18
Gebass Rise							
7735	Manganese crust	1	1	0.10	42.5	0.70	1.66
7736	Basalt	1	1	6.77	0.13	22.8	0.83
Koltso Mount							
7766	Manganese crusts	3	4	(0.20, 1.77) 0.85	(35.7, 42.2) 39.4	(0.40–5.90) 2.89	(0.45, 1.02) 0.70
7749	Basalt	1	1	6.45	0.07	22.1	0.80

If there is more than one analysis for one station, the minimum and maximum values are given in parentheses with commas, and the average value is given below the parentheses. The full chemical composition of FMFs and volcanic rocks is given in the Supplementary Information.

polish thin section of FMFs and volcanic rocks using a JXA-8100 (JEOL, Japan) microprobe with an energy dispersive spectrometer according to the proven scheme [12]. The detection limit of elements by the microprobe ranged from 0.04 to 0.1 wt %. To control the quality of analysis, a nonassembled set of standards from natural and synthetic materials was used. The error of determination did not exceed ±10 rel. % at an element content of 1 wt % and decreased at the higher content. Genetic constructions for FMFs were performed using geochemical data on the basis of previously developed diagrams [18, 19].

RESULTS AND DISCUSSIONS

As a result of this study, the presence of hydrothermal matter in the FMFs of the Sea of Japan was confirmed (Fig. 3). The average content of germanium in FMFs is high (12 g/t), the distribution is uneven (standard deviation S is 18.2 g/t) (Table 1). Among the samples with a near-clarke content (predominantly

Table 2. Results of germanium determination in standard samples of FMFs and rocks, g/t

No.	Standard sample	Attested (a) and compiled * (c)	Found X ($n = 5$)	RSD, %
1	NOD-A-1 (manganese nodule), United States	<0.5 (c)	0.63 ± 0.04	2.87
2	NOD-P-1 (manganese nodule), United States	0.54–1.09 (c)	1.06 ± 0.29	17.87
3	JB-3 (BASALT), Japan	1.19–1.23 (c)	1.27 ± 0.29	11.65
4	GSO 8670-2005 (SGD-2a, essexite gabbro), Russia	1.3 ± 0.2 (a)	1.37 ± 0.13	4.86
5	GSO 3333-85 (SG-3, granite), Russia	2.2 ± 0.4 (a)	2.23 ± 0.26	6.10

* Compiled values are taken from the GeoReM Internet resource [16].

manganese crusts on basalts), germanium-rich samples with the content up to 96 g/t (predominantly ferruginous crusts on andesites and rhyolites) were identified. The content of germanium in the germanium-rich samples is several times higher than the maximum values known to us for FMFs (15 and 19 g/t) [6, 20] and tens of times higher than a clarke number (from 1.3 to 1.6 g/t) [7]. It was previously shown that manganese crusts are generally composed of todorokite and birnessite, and ferruginous crusts are basically composed of goethite [10–12]. In the studied samples of volcanic rocks of the Sea of Japan, the germanium content averages 1.09 g/t; the distribution is characterized by low-variability, despite the presence of rocks with different silica contents in a sample—basalts, andesites, and rhyolites (standard deviation S is 0.18 g/t). The low variability is consistent with the existing concepts about the rather uniform distribution of germanium in different types of igneous rocks [2].

The results of statistical analysis indicate that the main factor controlling the content of trace elements in FMFs of the Sea of Japan is preferential/selective coprecipitation or sorption on iron oxyhydroxides and manganese of a different origin (Fig. 4a, groups I and II, respectively). The presence of a positive correlation of germanium with iron (r_{Ge-Fe}: 0.61) and a negative correlation with manganese (r_{Ge-Mn}: –0.52) indicates the accumulation of germanium on iron oxyhydroxides. The main factor controlling the germanium content in volcanic rocks underlying FMFs is probably the silica content in these rocks (Fig. 4b, Groups I and II). Germanium belongs to the silica group (r_{Ge-Si}: 0.66) and potassium (r_{Ge-K}: 0.70). Rubidium (r_{Ge-Rb}: 0.64), uranium (r_{Ge-U}: 0.67), thorium (r_{Ge-Th}: 0.72), and light rare earth elements ($r_{Ge-(La-Nd)}$: 0.68–0.77) are in the same group. Germanium has a negative correlation with all elements of the magnesium and Fe group.

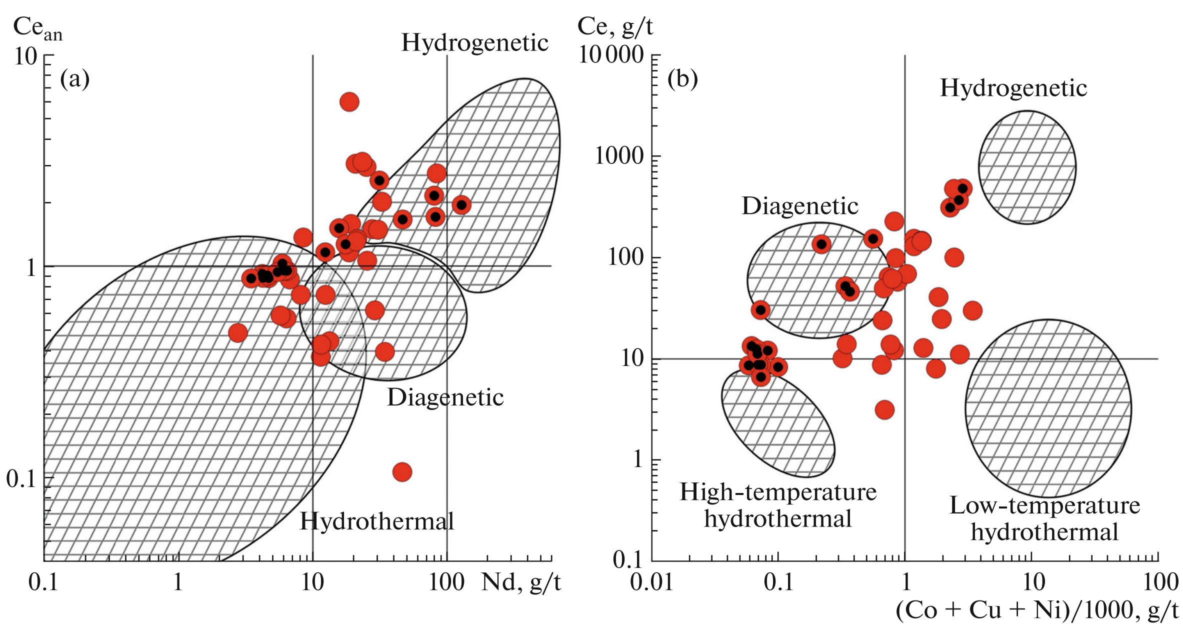

Fig. 3. Position of FMFs of the Sea of Japan (red circles) on genetic diagrams (a) [18] and (b) [19]. Black dots indicate samples with the germanium content ≥15 g/t. The full chemical composition of the FMFs is given in the Supplementary Information.

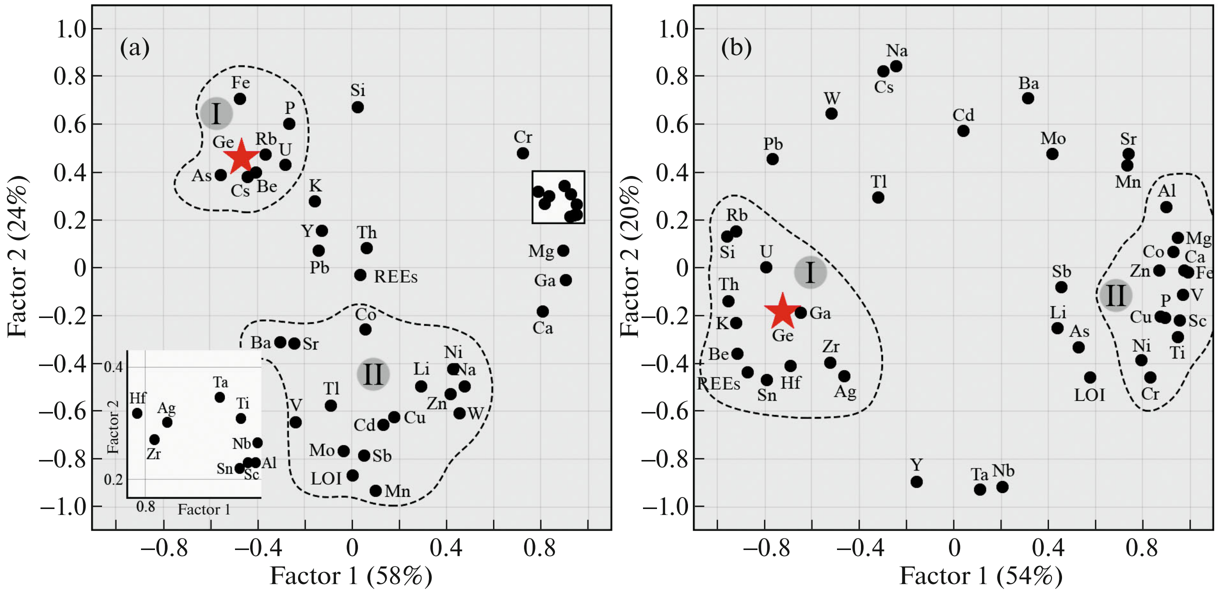

Fig. 4. Plots of the factor loading for germanium, other chemical elements, and loss on ignition (LOI) in (a) FMFs and (b) volcanic rocks of the Sea of Japan. The main groups of elements are highlighted with a dotted line; their numbers, with Roman numerals (I, iron group; II, manganese group). The position of germanium is marked with an asterisk. The full chemical composition and correlation matrices for FMFs and volcanic rocks are given in the Supplementary Information.

During the microprobe analysis, no mineral phases containing germanium were recorded in FMFs and volcanic rocks of the Sea of Japan. Apparently, germanium is present in the dispersed state in an amount not reaching the detection limit of the instrument. The latter is consistent with the generally accepted scientific concepts, according to which germanium belongs to rare dispersed elements and is found in nature generally in the form of impurities in rocks and minerals [2].

CONCLUSIONS

Summarizing the results of this study, we can conclude that the discovery of germanium-rich ferruginous crusts among the FMFs of the Sea of Japan, formed with the participation of a hydrothermal source of matter, increases interest in further study of germanium behavior in metal-rich deposits and, in particular, in hydrothermal ferruginous crusts. At present, in the general group of oceanic and marine FMFs, the hydrothermal ore crusts strongly rank below the nonhydrothermal deep-sea ferromanganese concretions and cobalt-rich manganese crusts in the mineral resource potential.

SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at https://doi.org/10.1134/S1028334X24604516.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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