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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 are dredged together with intermediate and acid volcanic rocks, are composed predominantly of iron oxyhydroxides (goethite) and contain germanium in a dispersed state.

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

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## INTRODUCTION

The Russian Academy of Sciences, together with other departments, in order to ensure the technological sovereignty of the country, has been tasked with determining the priorities for the long-term development of the mineral resource base of solid minerals. Germanium is included in the list of the main types of strategic mineral raw materials and, therefore, is in the area of priority attention [1]. At the current stage of study, the main sources of germanium are considered to be stratiform polymetallic and brown coal deposits (the germanium content in sphalerite exceeds 100 g/t, in coal – 200 g/t) [2, 3].

Ferromanganese nodules and crusts (ferromanganese formations, FMF) on the ocean and sea floor are solid minerals and 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 FMF. The few publications concern diagenetic, sedimentary (sedimentary, hydrogenic), sedimentary-diagenetic FMF and indicate a generally low germanium content at the level of 1–2 g/t [4-6], which approximately corresponds to the clarke for the upper part of the continental earth's crust. The clarke, according to various estimates, ranges from 1.3 to 1.6 g/t [7]. There are reasons to assume germanium enrichment in hydrothermal FMF. The element content in postmagmatic high-temperature aqueous fluids and mineral-forming solutions that formed hydrothermal mineralization of various deposits averages 17 g/t with a maximum value of 930 g/t [8]. The germanium dispersion halo in water is a reliable indicator of hydrothermal solution discharge onto the seabed [9].

The purpose of our study is to investigate the distribution characteristics of germanium in FMF formed with the participation of a hydrothermal source of matter.

## MATERIALS AND METHODS

The material for the study consisted of 29 samples of FMF from the summit parts of volcanic edifices in the Sea of Japan and 9 samples of volcanic rocks that compose these structures (Fig. 1, 2; Table 1). The material was dredged during the cruises of the R/V "Pervenets" in 1975–1980 and partially studied [10-12]. The Sea of Japan is located in the continent-ocean transition zone and is known for intense volcanic and post-volcanic hydrothermal activity. FMFs developed on volcanic edifices of the Sea of Japan have a hydrothermal-sedimentary origin [13] and are associated with volcanic rocks of two formation-geochemical types: post-rift

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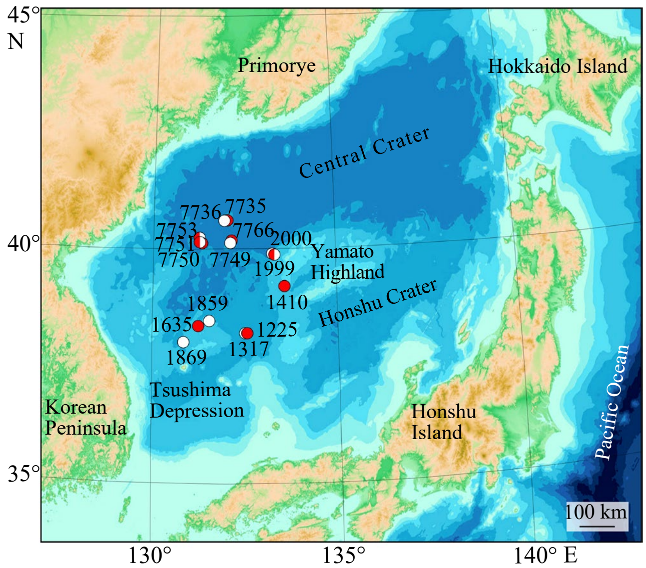


**Fig. 1.** Map of the Sea of Japan showing the largest morphological elements of the seafloor and dredging stations for FMFs (red circles) and volcanic rocks (white circles). Stations 1635, 1859, 1869 – Krishtofovich elevation. Stations 1410, 1999, 2000 – Northern Yamato Ridge. Stations 1225, 1317 – Galagan elevation. Stations 7735, 7736 – Gebass elevation. Stations 7750, 7751, 7753 – Evlanov elevation. Stations 7749, 7766 – Koltso mountain. The cartographic base is compiled according to GEBCO 2022 data.

(the absolute majority of FMFs) and marginal-continental [14]. Volcanic rocks of the post-rift type are mainly basalts. They form volcanic structures in deep-water basins with newly formed (sub)oceanic crust of Cenozoic age (mantle mafic volcanism). In our study, this type of volcanic rocks is represented by samples from the Galagan, Evlanov, Gebass, and Koltso elevations (Fig. 1; Table 1). Volcanic rocks of the marginal-continental type are mainly andesites, dacites, rhyolites, as well as trachydacites and trachyrhyolites. They form superimposed volcanic structures within large elevations with ancient Proterozoic-Mesozoic (sub)continental crust (crustal andesite-rhyolite volcanism). In our study, this type of volcanic rocks is represented by samples from the Krishtofovich elevation and the Northern Yamato Ridge (Fig. 1; Table 1).

Analytical studies were carried out at the Primorsky Center for Local Element and Isotope Analysis of the Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (Vladivostok). For elemental analysis, FMF samples and volcanic rocks were preliminary ground, dried at a temperature of 105–110°C to constant weight and subjected to open acid decomposition ($HF + HNO_3 + HClO_4$). The weight of the FMF samples was 30 mg, for volcanic rocks 50 mg. Loss on ignition (LOI) and silicon content in samples were determined by gravimetry, other macroelements by inductively coupled plasma atomic emission spectrometry using a Thermo iCAP 7600 Duo spectrometer (USA). The content of microelements, including germanium, was analyzed by inductively coupled plasma mass spectrometry on an Agilent 8800x quadrupole spectrometer (Japan) according to the previously proposed method [15], optimized for germanium. Germanium was determined by the isotope $^{74}Ge$. Polyatomic interferences from nickel, iron, potassium, and doubly charged rare earth elements were eliminated by background correction using the collision cell of the spectrometer filled with

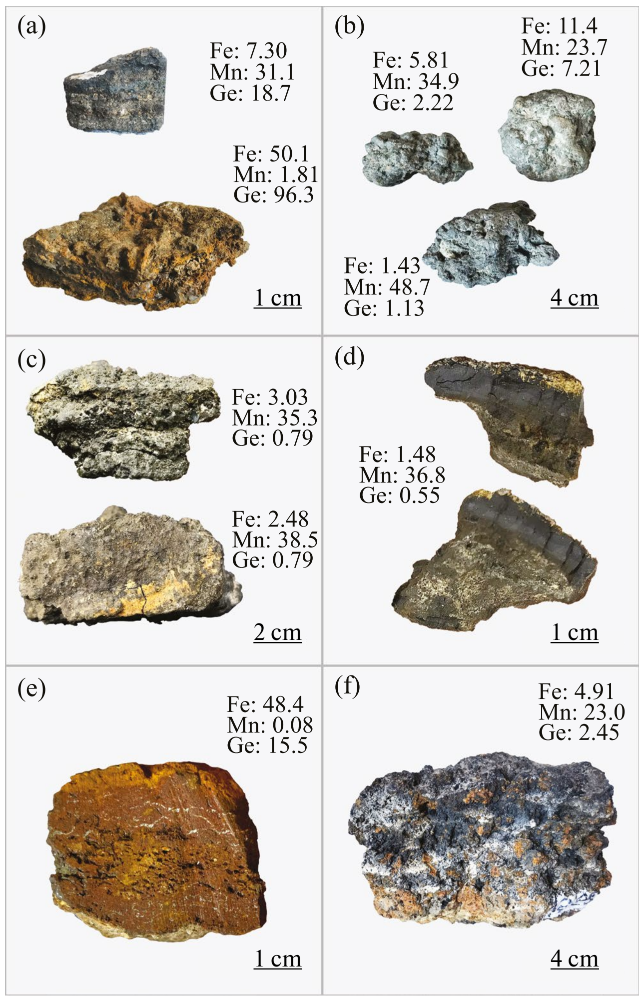


**Fig. 2.** General view of FMFs from the Sea of Japan with indication of average content of iron (wt. %), manganese (wt. %) and germanium (g/t). *a* – station 1635; *b* – station 1999; *c* – station 7753; *d* – station 7766 (view of the sample in chip); *e* – station 1410 (view of the sample in section); *f* – station 1225. For station locations, see Fig. 1.

**Table 1.** Content of iron, manganese, silicon and germanium in FMF and volcanic rocks of the Sea of Japan

| Station No. | Material type | Samples, *n* | Analyses, *n* | Fe, wt. % | Mn, wt. % | Si, wt. % | Ge, g/t |
|---|---|---|---|---|---|---|---|
| Krishtofovich Rise | | | | | | | |
| 1635 | Ferromanganese and ferruginous crusts and nodules | 5 | 7 | (6.63, 50.1)<br>24.7 | (1.81, 31.4)<br>19.8 | (4.4, 9.48)<br>7.01 | (15.9, 96.3)<br>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)<br>50.3 | (0.06, 0.15)<br>0.09 | (2.52, 9.13)<br>5.71 | (15.0, 17.1)<br>16.0 |
| 1999 | Ferromanganese and manganese crusts and nodules | 3 | 7 | (0.68, 16.2)<br>6.97 | (11.3, 50.7)<br>34.0 | (1.74, 18.2)<br>8.64 | (0.97, 7.85)<br>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)<br>15.3 | (1.76, 13.9)<br>7.83 | (21.4, 27.0)<br>24.2 | (8.31, 10.4)<br>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 | Predominantly manganese crusts | 4 | 8 | (0.14, 7.09)<br>2.21 | (28.0, 43.8)<br>38.0 | (0.51, 12.0)<br>4.70 | (0.55, 1.25)<br>0.82 |
| | Basalt | 1 | 1 | 7.82 | 0.08 | 21.8 | 1.12 |
| Galagan Rise | | | | | | | |
| 1225 | Ferromanganese crust | 1 | 3 | (1.64, 9.02)<br>4.91 | (7.65, 35.5)<br>23.0 | (4.42, 16.9)<br>10.2 | (2.33, 2.58)<br>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 Rise | | | | | | | |
| 7766 | Manganese crusts | 3 | 4 | (0.20, 1.77)<br>0.85 | (35.7, 42.2)<br>39.4 | (0.40-5.90)<br>2.89 | (0.45, 1.02)<br>0.70 |
| 7749 | Basalt | 1 | 1 | 6.45 | 0.07 | 22.1 | 0.80 |

Note. When more than one analysis is available for a station, the minimum and maximum values are indicated in parentheses separated by a comma, with the mean value below the parentheses. The complete chemical composition of FMF and volcanic rocks is provided in the appendix.

helium. Foreign and domestic standard samples of FMFs and rocks were used to control the quality of chemical element determination results (Table 2). The accuracy of element determination results was assessed by the values of the relative standard deviation (RSD). For macroelements, the error did not exceed 2–5%, for most microelements the RSD was 15–20% or less, for germanium less than 18% (Table 2), which meets the quality criteria for quantitative elemental analysis in geochemical studies [17]. Databases compiled for FMFs and volcanic rocks were processed using multivariate statistical methods (appendix). The correlation analysis established the relationships between germanium and other chemical elements. Taking into account the strongest positive relationships in the space of the main factors, geochemical groups were identified, and the position of germanium was noted. The search for germanium-containing mineral phases was carried out in polished sections of FMFs and volcanic rocks using a JXA-8100 microprobe (“JEOL”, Japan) with an

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

| No. | Standard sample | Certified (a), compiled* (c) | Found X ( $n = 5$) | RSD, % |
|---|---|---|---|---|
| 1 | NOD-A-1 (manganese nodule), USA | < 0.5 (c) | 0.63 ± 0.04 | 2.87 |
| 2 | NOD-P-1 (manganese nodule), USA | 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 |

Note. * − Compiled values are taken from the GeoReM internet resource [16].

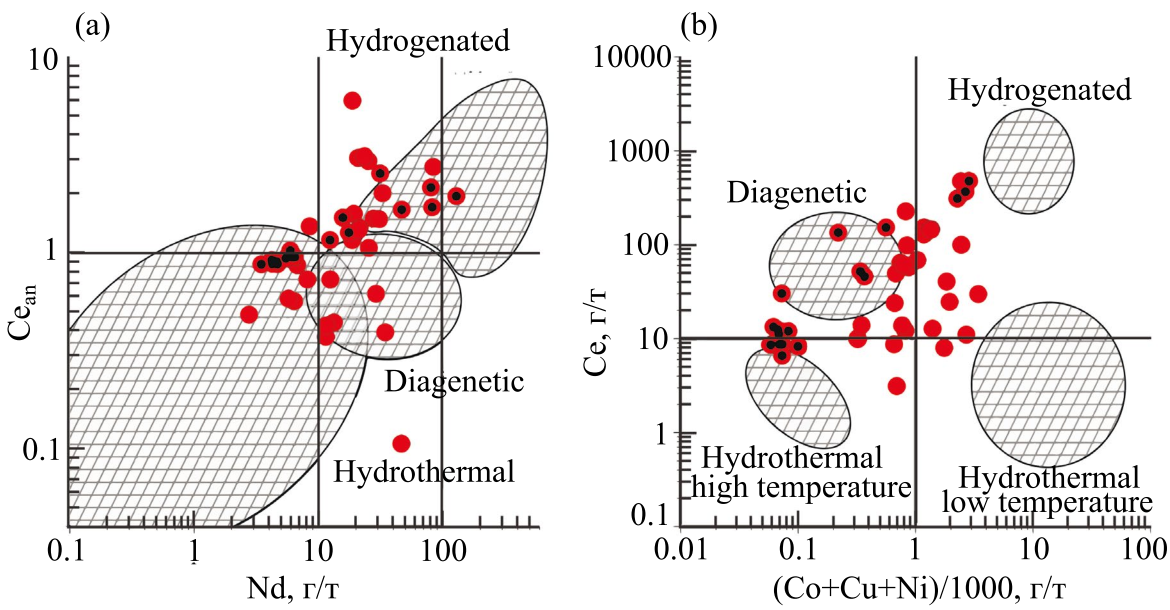


**Fig. 3.** Position of ferromanganese formations from the Sea of Japan (red circles) on genetic diagrams [18] *(a)* and [19] *(b)*. Black dots mark samples with germanium content ⩾ 15 g/t. The complete chemical composition of ferromanganese nodules is provided in the appendix.

energy-dispersive spectrometer according to an established scheme [12]. The detection limit of elements by the microprobe ranged from 0.04 to 0.1 wt. %. A non-built-in set of standards from natural and synthetic materials was used to control the quality of the analysis. The determination error did not exceed ± 10 rel.% with an element content of 1 wt. % and decreased with higher content. Genetic constructions for FMFs were performed based on geochemical data using previously developed diagrams [18, 19].

## RESULTS AND DISCUSSION

The conducted research confirmed the presence of hydrothermal material in ferromanganese nodules of the Sea of Japan (Fig. 3). The average content of germanium in FMF is high (12 g/t), distribution is uneven (standard deviation $S$ – 18.2 g/t) (Table 1). Among samples with near-clarke content (predominantly manganese crusts on basalts), high-germanium samples with content up to 96 g/t (predominantly ferruginous crusts on andesites and rhyolites) were identified. The germanium content in high-germanium samples is several times higher than the maximum values known to us for FMF (15 and 19 g/t) [6, 20] and tens of times higher than the clarke (from 1.3 to 1.6 g/t) [7]. It was previously shown that manganese crusts are composed mainly of todorokite and birnessite, while ferruginous crusts are composed of goethite [10-12]. In the studied samples of volcanic rocks from the Sea of Japan, the average germanium content is 1.09 g/t; the distribution shows little variation despite the presence of rocks with different silicon content in the sample – basalts, andesites, and rhyolites

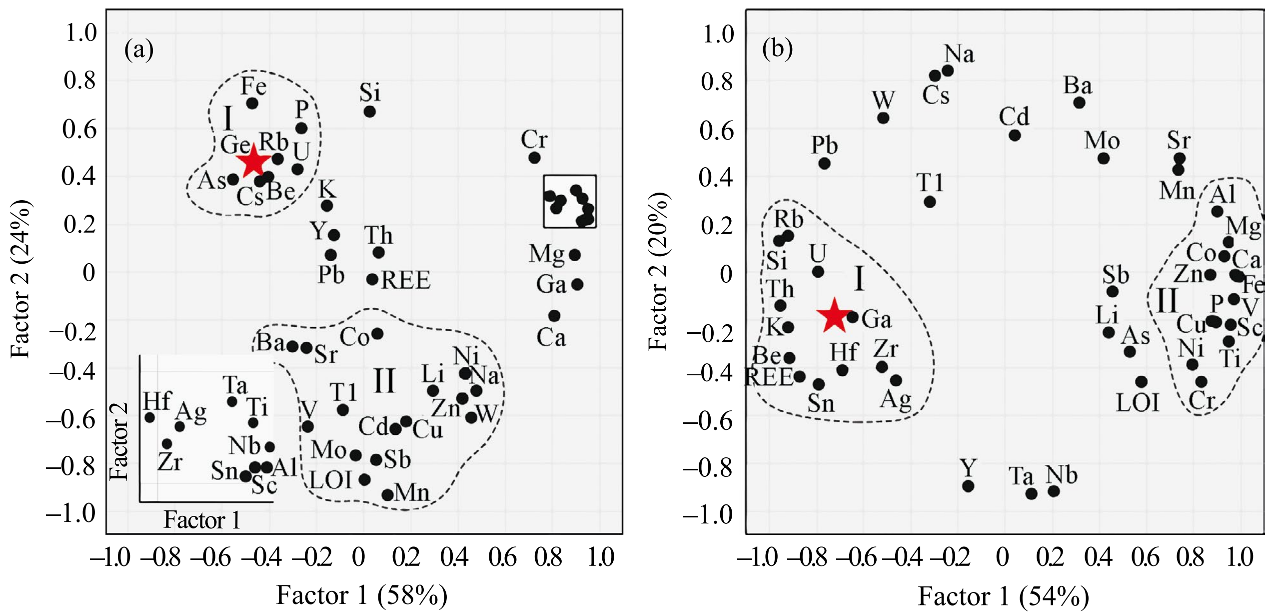


**Fig. 4.** Factor loading plots for germanium, other chemical elements, and loss on ignition (LOI) in FMF *(a)* and volcanic rocks *(b)* of the Sea of Japan. The main groups of elements are highlighted by a dotted line, their numbers are indicated by Roman numerals (I – iron group, II – manganese group). Germanium position is marked with an asterisk. The complete chemical composition and correlation matrices for FMF and volcanic rocks are provided in the appendix.

(standard deviation $S$ – 0.18 g/t). The low variability is consistent with existing ideas about the fairly uniform distribution of germanium in various types of igneous rocks [2].

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

During microprobe analysis in FMF and volcanic rocks of the Sea of Japan, no mineral phase containing germanium was recorded. Obviously, germanium is present in a dispersed state in an amount that does not reach the detection limit of the instrument. The latter is consistent with generally accepted scientific concepts, according to which germanium belongs to rare dispersed elements and is found in nature mainly as impurities in rocks and minerals [2].

## CONCLUSION

Summarizing the results of the conducted research, it can be concluded that the discovery of high-germanium ferruginous crusts among the FMF of the Sea of Japan, formed with the participation of a hydrothermal source of matter, increases interest in further studying the behavior of germanium in metalliferous deposits and, in particular, in hydrothermal ferruginous crusts. Currently, in the general group of oceanic and marine FMF, hydrothermal ore crusts are significantly inferior in mineral resource potential to non-hydrothermal deep-sea ferromanganese nodules and cobalt-bearing manganese crusts.

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